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3,424,545  
**LAUNDERING ADJUNCT AND METHOD  
 OF PREPARING**

Robert Andrew Bauman, New Brunswick, N.J., assignor  
 to Colgate-Palmolive Company, New York, N.Y., a  
 corporation of Delaware  
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**ABSTRACT OF THE DISCLOSURE**

A home laundering process using an aqueous detergent which provides the presence of phosphorylated cellulose (containing about 5.3% phosphorus) in the wash cycle to sequester the calcium and magnesium ions in the water.

The present invention relates to sequestering calcium and magnesium ions in home laundering and, more particularly to a laundering adjunct, a method of preparing said adjunct, and to a method of using said adjunct in home laundering.

The effect of water-soluble calcium and magnesium salts in the water used in laundering or in personal ablutions has been recognized so widely it hardly seems necessary to refer to it. For commercial laundries commercial water-softening units and regenerating facilities are available. For the home laundry similar regenerable water-softening units are available. However, the use of the home-size regenerable water-softening units is not universal and, in fact, in many localities such water-softening units are not available or are beyond the comprehension of a large portion of the population.

To overcome these difficulties and to make a better product the manufacturers of detergents and soap powders and even the manufacturers of both salts have incorporated in their products exhaustible agents such as the so-called inorganic detergency builders.

The role of the inorganic builder in improving the performance of a detergent formulation is of the highest importance, but the mode of action is still not clear. A number of functions have been suggested for it, including suspending of particulate soils, lowering the critical concentration of the detergent, increasing the wetting rate, influencing the degree of adsorption of surfactant on textile fibers, effecting the electrostatic charge of soil and fabric, and others but the major effects are usually attributed to the water softening ability of the inorganic builder.

Formulation of a detergent to take care of all of the hardness in the water used in the wash step of the laundry cycle is not difficult except in the case of liquid detergents where it is a real problem to combine the necessary quantities of detergent, builder, and other essential ingredients into a compatible mixture occupying a reasonable final volume. In this case an alternate method for achieving the benefits of a builder would be a boon to the formulator and manufacturer.

Since at present the inorganic builder or other water-softening agent is incorporated in the detergent, a part of the detergent formulation and water-soluble, it is available only during the wash step and not during the rinse step or steps of the laundering cycle. It has been shown that the residual-soil build-up on repeatedly laundered cotton can be removed by a rinse containing ethylene diamine tetraacetate (EDTA) which is an indication of the desirability of maintaining a useful concentration of water-softening agent during the rinse portion of the laundering cycle as well as during the wash portion thereof.

Thus, it is apparent that the present means of over-

coming the disadvantages of the variation of the hardness of the water in various parts of the world are (1) limitation of the formulation of liquid detergents; (2) the absence of water-softening agent in the rinse cycle; and (3) the relative complexity of the regeneration operation of home water-softening units. The present invention overcomes all of these disadvantages.

At the present time the generally used water-softening agents incorporated in home laundering detergents are complex phosphates such as sodium tripolyphosphate, i.e., penta-sodium tripolyphosphate, and potassium pyrophosphate. The present invention provides a laundering adjunct to be used in conjunction with detergents containing inorganic builder or in conjunction with detergents substantially devoid of inorganic builder in the washing step and in the rinsing step of a home laundering cycle and in some forms for use in personal ablutions.

Accordingly, it is an object of the present invention to provide water-insoluble geometric solid comprising cation-exchange material suitable for contact with wash- and rinse-water during both portions of a home laundering cycle. It is a further object of the present invention to provide a water-insoluble foraminous sheet of fibrous material having cation-exchange capabilities. It is also within the purview of the present invention to provide the inner periphery of a home laundering machine or the dasher thereof with a continuous or discontinuous surface of cation-exchange material bonded to the structural material by water-insoluble material. It is a preferred object of the present invention to provide phosphorylated cellulose having water-softening capabilities for contact with wash- and rinse-water in both the wash portion and the rinse portion of home-laundering cycle. It is also an object of the present invention to provide a method of using such water-insoluble cation-exchange materials in both the wash and rinse portions of a home-laundering cycle. The present invention provides a method of preparing phosphorylated cellulose for use as a water-softening agent in the wash and rinse portions of a home-laundering cycle. A method regenerating a phosphorylated cellulose water-softening material is likewise an object of the present invention.

It is to be observed that, while industrial size water-softening plants employing zeolites have been available for at least forty years, cation-exchange resins have been available for at least twenty years, and domestic water-softening units have been available for at least fifteen years, no one has suggested that the growing children in a home can have the advantage of the presence of calcium salts in the potable water of the domestic environment and the home laundress can have the advantage of soft water by the method of the present invention.

In 1956 U.S. Patent No. 2,749,306 issued to W. B. Coleman in which was disclosed a method of regenerating water-softening ion-exchange materials including the removal of iron salt deposits. The patentee found that alkali metal phosphates were very useful for the regeneration of ion-exchange material and particularly recommended the alkali metal pyro-, poly-, and metaphosphates and acid phosphates or mixtures of the foregoing for that purpose. The preferred phosphates were the alkali metal tripolyphosphates, such as sodium tripolyphosphate, and the pyrophosphates such as sodium acid pyrophosphate.

While the early development of ion-exchange materials was directed primarily to the use of zeolites, however, in 1931 U.S. Patent No. 1,793,670 issued to G. Borrowman disclosing an ion-exchange organic material comprising lignite or brown coal having exchangeable alkali metal. Further development of organic ion-exchange material is evidenced by the issuance of U.S. Patent No. 2,148,970 disclosing a process of liquid purification by contacting

the liquid with a water insoluble solid cyclic organic compound having an imino group within the ring and adjacent thereto an atom which is double bonded to a third atom.

In 1940 U.S. Patent No. 2,195,196 issued to H. Wassenecker et al. disclosing a method for diminishing the swelling of phenol resins in aqueous solutions. The resinous gel produced by condensing a phenolic body with more than a molar equivalent of an aldehyde is subjected to an after-treatment with a large quantity of hot concentrated hydrochloric sulfuric or phosphoric acid. In 1940 U.S. Patent No. 2,204,539 issued to H. Wassenecker et al. which was directed to a method of effecting cation-exchange employing a water-insoluble resin of an aldehyde and a member of the group consisting of naphthalene, acenaphthene, hydroxybenzene, and phenanthrene containing nuclear sulfonic acid groups.

In U.S. Patent No. 2,340,111 an ion-exchange resin comprising infusible, insoluble copolymer containing carboxyl groups is disclosed. In U.S. Patent No. 2,366,007 sulfonated, cross-linked, insoluble, infusible polymerizates of polyvinyl aryl compounds are disclosed for use in removing cations from liquid media, especially aqueous media. The cation-exchange resin disclosed in U.S. Patent No. 2,373,547 is the infusible resinous reaction product of phenol, formaldehyde, and an aliphatic amino-carboxylic acid. In the companion U.S. Patent No. 2,373,549 a resin having high cation capacity comprising a phenol, aldehyde, nitrourea reaction product is described. The disclosure of U.S. Patent No. 2,611,337 is concerned with cellulose - nitrogen - and phosphorous-containing materials having the property of exchanging cations in aqueous solutions. A method removing cations from water employing substantially spherical beads having diameters in the range of 0.3 to 1.0 millimeter comprising the reaction product of methacrylate, divinylbenzene, and methacrylic anhydride has been disclosed.

In U.S. Patent No. 2,933,460 issued in 1960 to G.A. Richter, Jr. et al. ion-exchange fibers having at least one small dimension of the order of one-tenth to twenty mils are described. These fibers comprise a cross-linked polymer of a linear addition polymer at least seven mol percent of the units containing ion-exchange groups such as carboxyl groups, sulfonic groups, phosphoric acid groups, and thiol groups for cation-exchange. A companion U.S. Patent No. 2,974,101 provides a description of improved ion-exchange assemblies and of methods of treating liquids particularly assemblies comprising filamentous structures. Similar to the latter patent is the disclosure of U.S. Patent No. 3,062,379 which is directed to fabricated ion-exchange fiber constructions in which relatively short sections of ion-exchange fibers are attached to a supporting base composed in whole or in major part of water-insoluble materials which do not exhibit ion-exchange properties.

The further disclosure of fiber-form ion-exchange materials is provided in U.S. Patent No. 3,097,051. These fiber-form ion-exchange materials native fiber cellulose is reacted in a system comprising trifluoroacetic anhydride, a suitable inert non-aqueous solvent or diluent and the mono-anhydride of a tricarboxylic non-aqueous organic acid which contains one free, active carboxylic group in addition to the carboxylic groups involved in the cyclic anhydride structure.

In U.S. Patent No. 2,609,360 it is stated that water-soluble phosphates of polyvinyl alcohol are produced by the reaction of polyvinyl alcohol with urea phosphate. These are capable of self-polymerization, when heated without the aid of a catalyst, to form high-capacity ion-exchange substances.

In Textile Research Journal for January, 1949, J. F. Jurgens, J. David Reid, and J. D. Guthrie published a paper entitled "Phosphorylated Cotton Cellulose as a Cation-Exchange Material." The essence of the publication is that phosphorylated cotton cellulose made by the phosphoric acid-urea (see U.S. Patent No. 2,482,755) has

a high cation-exchange capacity and when used in the form of a coarse fabric it shows good flow characteristics in the calcium-hydrogen cycle. Its cation-exchange capacity increases with increasing phosphorus content and at a phosphorus content of about five percent the cation-exchange capacity reaches about 1,000 milliequivalents per kilogram. It is possible that specialized uses may be found for phosphorylated cotton cellulose, especially in the cotton form. Subsequently, J. D. Guthrie published an article in Industrial and Engineering Chemistry (Vol. 44, No. 9) entitled "Ion Exchange Cottons" in which the preparation of cation-exchange cottons is described. The product was made by the method described in U.S. Patent No. 2,482,755 by curing cotton with a mixture of phosphoric acid and urea. Sulfoethylated cotton, partially carboxymethylated cotton, and the succinic acid half ester of cotton cellulose, all having cotton-exchange capabilities, are also described. "Continuous Ion Exchange With an Endless Belt of Phosphorylated Cotton" is the title of an article published in the March 1955 issue of Industrial and Engineering Chemistry.

In spite of all of the investigations of cation-exchange material in the last two decades no one has suggested a simple method of applying the principles of cation-exchange to home laundering operation. The present invention provides (1) for hanging a cation-exchange fabric in a traditional tub used for hand washing and/or rinsing or in the modern automatic washing machine during both the wash and the rinse portions of the laundering cycle; (2) for coating in any suitable manner the periphery of the traditional tub used for hand washing and rinsing or the periphery of the tub of a modern automatic washer in a continuous or discontinuous form with cation-exchange material; (3) for coating in any suitable manner in a continuous or discontinuous fashion the exterior of the dasher of an automatic washing machine; and (4) for suspending in the traditional tub used for hand laundering or in the modern automatic washer during both the wash and rinse cycles a porous container charged with particulate cation-exchange material and for personal ablutions a wash-cloth comprising two layers of terry cloth and an interposed layer of fabric having cation-exchange capabilities.

It is to be observed that the ion-exchange capacity of ion-exchange materials is not the same. Guthrie in Tex. Res. J. 20, 617 (1950) and Ind. Eng. Chem. 44, 2188 (1952) examined the capacities for the exchange of hydrogen for sodium atoms (but not for calcium binding) of cotton upon which ion-exchange properties had been conferred in several ways. The results are summarized in Table I.

TABLE I

Material:	Capacity in meq./g. <sup>1</sup>
Phosphorylated cellulose -----	2.56
Sulfethoxy cellulose -----	0.340
Carboxymethyl cellulose -----	0.248
Succinic acid half ester of cellulose -----	0.247

<sup>1</sup> Milliequivalents per gram.

These data clearly show that for the exchange of hydrogen for sodium the capacity of phosphorylated cellulose is about seven and one-half to ten times that of the other materials or 750 to 1000 percent that of the other cellulosic materials.

Illustrative of the principles of the present invention is the preparation of phosphorylated cellulose to provide a cation-exchange material, and the use of the so-produced cation-exchange material to sequester calcium ions under conditions comparable to those existing in home laundering.

Preparation of phosphorylated cotton containing 5.3% of phosphorus

A 24 x 6 inch strip of "Indianhead" cotton was evenly impregnated with a solution of 13.5 grams of urea and 6

grams of 86% phosphoric acid in 16 milliliters of water. This amount of solution was just sufficient to impregnate the cloth. The cloth was air-dried in a horizontal position and then heated for thirty minutes at about 140° to 150° C. (about 285° to about 305° F.) in a gravity convection oven. The treated cloth was washed repeatedly in deionized water, dilute aqueous sodium hydroxide, water and then air-dried. The treated cloth so obtained is nearly white, but has a rougher, heavier hand than the original cloth, and, when wet, it has a slippery feel. Under agitation of a "Terg-O-Tometer" run the cloth frays badly at the edges. For the detergency tests three ways of preventing the disintegration were employed to wit: (1) phosphorylating a sulfone-crosslinked cotton fabric instead of "Indianhead" cotton (Test 1); (2) painting the edges with a label varnish (Test 2); and (3) hemming the four edges (Test 3). Cotton crosslinked with "Ganalok A-14" (sulfone crosslinked cotton) was phosphorylated satisfactorily to a product of markedly greater strength than "Indianhead" cotton, but its capacity for calcium was much lower. The varnished edge cloth successfully withstood the agitation of the "Terg-O-Tometer" machine, but its calcium capacity was reduced out of proportion to the actual area covered by the varnish. Hemming proved to be the preferable protective treatment.

Assuming that the reaction which occurs is the conversion of the hydroxyl groups of cellulose to phosphoric ester groups,  $-O-PO(ONa)_2$  then the sample of phosphorylated "Indianhead" cotton which was found to contain 5.3 percent of phosphorus represents a ten percent conversion of the available hydroxyl groups of the cotton to phosphoric ester groups. The capacity of the cloth containing 5.3 percent of phosphorus is about 30 milligrams of calcium per gram of cloth.

#### Calcium binding capacity

The capacity of the so-produced phosphorylated cotton to bind calcium was measured by agitating a weighed piece of the cloth in an aqueous solution of calcium chloride of known concentration and then determining the depletion of calcium ions in the solution by titration of an aliquot with standard ethylene diamine tetraacetate solution. [Betz, "Handbook of Industrial Water Conditioning," 5th Ed. Betz Laboratories Inc., (1957)].

The time required for the phosphorylated cotton to bind calcium to its fullest capability was dependent on the physical form, being fast for open textured cotton gauze and slow for the more tightly woven "Indianhead" fabric. Although for the latter material as much as 24 hours might be required for completion of the reaction, the rate of the reaction, as might be suspected, slows down considerably during this time so that most of the calcium binding occurs in an initial short period. One can, therefore, speak of a practical calcium binding capacity of the cloth meaning the calcium removed from solution during some arbitrary time period comparable to that encountered in laundering practice. In the following table is shown the time dependence of calcium binding by triplicate pieces of cloth each immersed in one liter of calcium chloride solution containing 60 mg. calcium ion—this is equivalent to 150 p.p.m. (as  $CaCO_3$ ) hard water.

TABLE II

Time	Mg. calcium bound		
	A	B	C
0.....	0	0	0
20 minutes.....	32	32	31
1 hour.....	42	35	38
2.5 hours.....	54	52	53
5 hours.....	57	57	57
24 hours.....	59	59	59

To determine whether the capacity is dependent on the concentration of calcium, equal weights of phos-

phorylated cotton (sulfone-crosslinked cotton in this case) were agitated for one hour in solutions of calcium chloride varying in concentration from 0.008 to 0.013 M (80–1300 p.p.m. as  $CaCO_3$ ), but in which the same total quantity of calcium was present. In each case the weight of calcium bound by the cloth was the same, indicating that it is the amount of calcium which is important and not its concentration.

Since substantially all soap powders contain sodium and/or potassium, e.g., in one commercial product 0.013 molal sodium and in another 0.003 molal sodium plus potassium the effect of sodium ion upon the capacity of the phosphorylated cotton to bind calcium was examined by agitating pieces of sulfone-crosslinked phosphorylated cotton weighing 300 milligrams in 25 milliliter portions of an aqueous solution containing varying amounts of sodium chloride and being 0.0126 molal to calcium chloride. The data presented in Table III clearly shows that at concentrations if sodium in the range usually existing in commercial detergents the interference of the sodium ion is not a serious factor in practice.

TABLE III

Concentration NaCl, M:	Mg. calcium bound/gram of cloth
0.00115 .....	16.3
0.0104 .....	16.1
0.1013 .....	10.3
1.017 .....	4.2

The regenerability of a calcium binding cloth will depend at least in part on the kind of reactive groups that it possesses. Thus, from recorded experience with ion exchange resins of varying types the ease of regeneration could be expected to vary from excellent with sulfonic acid groups to poor with carboxyls and of some intermediate character with phosphorus acid groups. In practice it was found that a 20% solution of sodium tripolyphosphate would restore all the calcium binding activity of exhausted phosphorylated cotton, but a sizable portion of the activity could be regained by the use of even 0.1% of this reagent. This was demonstrated repeatedly in an experiment in which three similar pieces of phosphorylated cotton (M, D, E) and one piece of untreated cotton (P) were alternately agitated in a Terg-O-Tometer with calcium chloride solution and with a 0.05% solution of sodium tridecylbenzenesulfonate containing for M, no other reagent; for P and D, 0.1% NaTPP; and for E, 0.2% NaTPP. Between treatments were rinses with deionized water. The remaining hardness of the calcium chloride solutions was determined after treatment with the cloth by EDTA titration, and the results in p.p.m. (as  $CaCO_3$ ) hardness removed from the original 150 p.p.m. water are tabulated below.

TABLE IV

Phosphorylated cotton sample.....	P	M	D	E
Regenerating solution:				
Sodium tridecylbenzenesulfonate, percent.....	0.05	0.05	0.05	0.05
Pentasodium tripolyphosphate, percent.....	0.1	.....	0.1	0.2
P.p.m. of hardness removed by cloth:*				
Originally.....	0	79	79	78
After saturation with calcium.....	0	1	2	0
After wash.....	0	5	58	71
After saturation with calcium.....	0	0	1	0
After wash.....	0	0	54	66
Do.....	0	5	62	75

\*P.p.m.—parts per million (parts per 10<sup>6</sup>).

It is evident that (1) untreated cotton (P) shows no calcium binding properties, (2) once the treated cloth has been saturated with calcium its activity cannot be restored by washing in 0.05% NaTBS alone, and (3) the relatively dilute solutions of NaTPP, similar to what would be present in the wash water during laundering, can restore a surprisingly large amount of capacity. These

experiments were run in deionized water; additional NaTPP would be necessary to take care of any hardness in the water that would be used in a practical application of this procedure.

Statistically controlled detergency tests were run in which it was possible to demonstrate a beneficial effect of a calcium binding cloth on detergency.

The test chosen was one in which a panel of eight persons each wiped his face and neck with four 4½ x 6 inch swatches of "Indianhead" cotton (two of these in the morning and two in the afternoon of the same day) for which instrumental reflectance readings were obtained before and after soiling. These swatches, separated into four lots drawn one from each panel member, were washed in various solutions in the four buckets of a Terg-O-Tometer for twenty minutes at 120° F. and 100 r.p.m. agitation, rinsed, pressed, and the reflectance again read.

This procedure was repeated twice more, the difference between the final reflectance reading and the initial reading on the fresh cloth being taken as the Residual Soil. Throughout these tests 0.05% sodium tridecylbenzenesulfonate was used in every bucket. The NaTPP used was Westvaco anhydrous commercial grade of 95% purity. All wash solutions were adjusted to pH 10 before use.

#### FIRST DETERGENCY TEST

##### Object

To measure the effect on detergency of phosphorylated cotton in the absence and presence of sodium tripolyphosphate.

##### Conditions

Phosphorylated crosslinked cotton with capacity of 50 mg. Ca or the equivalent of one liter of 125 p.p.m. (as CaCO<sub>3</sub>) hard water; 100 p.p.m. water for wash and rinse (made from CaCl<sub>2</sub>).

##### Results

Treatment	Residual soil	Significance, percent
(1) Detergent alone.....	14.41	} 95
(2) Detergent + P.C.*.....	11.48	
(3) Detergent + NaTPP(0.05%).....	4.52	} 70
(4) Detergent + NaTPP + P.C.....	4.26	

\*P.C.=phosphorylated cotton.

##### Conclusions

The phosphorylated cotton is effective in reducing residual soil buildup. There is a small improvement when P.C. is present in addition to NaTPP.

#### SECOND DETERGENCY TEST

##### Object

To determine whether improved performance of phosphorylated cotton can be obtained by (1) using cloth of higher capacity, (2) adding a neutral electrolyte, and (3) pretreating the wash solution with the calcium binding cloth.

##### Conditions

Phosphorylated Indianhead cotton (with edges protected by Varniton V-21B Label Varnish) with capacity of 38 and 56 mg. Ca or equivalent to one liter of 95 and 140 p.p.m. hard water; 100 p.p.m. hard water for wash, deionized water for rinse.

##### Results

Treatment	Residual soil	Significance, (percent)
(1) P. C. for 95 p.p.m. hardness.....	7.16	} 90
(2) P. C. for 140 p.p.m. hardness.....	5.94	
(3) P. C. as in 1 + 0.1% Na <sub>2</sub> SO <sub>4</sub> .....	3.81	} 99
(4) P. C. as in 2, and ten minutes pretreatment of wash solutions.....	3.84	

#### Conclusions

All three variations yield improved performance of phosphorylated cotton. Ranked in order of decreasing importance they are (1) added electrolyte, (2) pretreatment of wash solution, and (3) increased capacity of P.C.

#### THIRD DETERGENCY TEST

##### Object

To determine whether a combination of all three factors found individually to improve the performance of phosphorylated cotton will give detergency building equivalent to that of sodium tripolyphosphate.

##### Conditions

Phosphorylated Indianhead cotton with hemmed edges with capacity of 60 mg. and 150 mg. Ca or equivalent to one liter of 150 p.p.m. and 385 p.p.m. hard water; 150 p.p.m. hard water for wash, deionized water for rinse; fifteen minute pretreatment of wash solution with P.C.

##### Results

Treatment	Final Hardness p.p.m. <sup>1</sup>	Residual Soil	Significance percent
(1) 0.1 % Na <sub>2</sub> SO <sub>4</sub> .....	131	6.11	} 99
(2) Na <sub>2</sub> SO <sub>4</sub> + P.C. <sup>2</sup> for 150 p.p.m. hardness.....	36	3.03	
(3) Na <sub>2</sub> SO <sub>4</sub> + P.C. for 385 p.p.m. hardness.....	10	2.65	} 70
(4) 0.075% NaTPP.....	-----	1.89	

<sup>1</sup> Average of three runs.

<sup>2</sup> Phosphorylated Cotton.

#### Conclusions

Pretreatment of the wash solution with phosphorylated cotton of higher than rated capacity in the presence of a neutral electrolyte actually binds calcium ions in use and gives performance approaching that of NaTPP.

These data obtained in a statistically-controlled "Terg-O-Tometer" test show that calcium ions are bound by phosphorylated cotton under washing conditions and that the performance approaches that of sodium tripolyphosphate as measured by residual soil on the swatches after the three cycles.

These data also establish that after saturation with calcium ions the phosphorylated cotton, i.e., the exhausted cation-exchange material, can be regenerated by soaking in pentasodium tripolyphosphate solution having a concentration of NaTPP as low as one percent.

The simplest form of a home laundering insoluble regenerable sequesterer for calcium and magnesium, i.e., a cation exchange material, is a non-ravelling cloth having an area of at least about one square foot impregnated with a water-insoluble material having alkaline earth binding groups, e.g., carboxylic and/or sulfonic and/or phosphoric acid groups. The phosphorylated cotton described and discussed herein before is illustrative of this embodiment of the present invention. Since the capacity of phosphorylated cotton containing about 5.3 percent of phosphorus is about 30 milligrams per gram and since 60 milligrams of calcium per liter is a hardness of about 150 p.p.m. it is a simple mathematical computation, knowing the volume of the tub or automatic washer and the hardness of the water used, to calculate for phosphorylated cotton the size or weight of cation-exchange material required to have a practical affect upon the sequestration of cations in the water employed in the wash and/or rinse portion of the laundering cycle. For example, with phosphorylated cotton containing 5.3 percent of phosphorus having a calcium binding capacity of 30 milligrams per gram of cloth and water having a hardness equivalent (as CaCO<sub>3</sub>) to 150 p.p.m. or 60 milligrams per liter, i.e., about 227 milligrams per gallon, about 7.6 grams of the

phosphorylated cotton per gallon of water is used. With similar knowledge of the sequestering power of other cation-exchange materials the amount required can be readily calculated. Consequently, for the phosphorylated cotton described hereinbefore for use in the wash and the rinse portions of the laundering cycle without regeneration between the wash and rinse portions of a laundering cycle consisting of a wash portion and two rinse portions each employing 17 gallons of water having a hardness of 150 p.p.m., about 386 grams of phosphorylated cotton is used with regeneration with TPP solution of at least one percent concentration after each laundering cycle. When TPP or other regenerant is present in the wash portion of the laundering cycle regeneration is less frequent. For improved results the water used in either the wash portion or the rinse portion or in both portions of the laundering cycle is pretreated with phosphorylated cotton, of higher than the minimum required, in the presence of a neutral electrolyte, e.g., sodium sulfate.

Many persons prefer to perform their ablutions using soft water. For those forced to use hard water, a wash cloth comprising a sandwich of terrycloth, for example, with cation-exchange material, for example phosphorylated cotton interposed between two layers of terrycloth and hemmed around the edges solves the problem in a simple manner.

In another embodiment of the present invention particulate cation-exchange material is charged to a porous container, e.g., a loosely woven bag with a draw-string closure, which charged container is attached to the water inlet of an automatic washer or suspended therein in any other suitable manner.

In still another embodiment of the present invention a portion or the whole of the inner periphery of tub of a washing machine is coated with a water-insoluble adhesive and then coated with particles of cation-exchange material or with a layer of cation-exchange fabric. Alternatively, the plunger or dasher can be so treated and when desired both the dasher and the inner periphery of the tube are so treated.

It is manifest that the incidence of regeneration of the water-insoluble cation-exchange material is dependent upon (1) the hardness of the water employed, i.e., the milligrams of cation to be removed per gallon of water; (2) the volume of water employed; (3) the cation-binding capacity of the cation-exchange material per gram; and (4) the quantity or weight of cation-exchange material employed.

Those skilled in the art will understand that when a detergency builder such as pentasodium tripolyphosphate is present in the detergent formula that a mobile equilibrium is established and the incidence of regeneration of the cation-exchange material is less frequent.

Heavy duty liquid detergent formulations have always had two major drawbacks in attaining a sizeable share of the market; one is cost and the other is their failure to measure up to the performance of powdered detergents especially in hard water. The major factor in the failure of heavy duty liquids to achieve performance parity with powders is the difference in builder content. Solubility limits have set the builder content in liquids at about 20% while powders incorporate approximately 50% builder. Detergent raw material suppliers as well as detergent formulators have been aware of the problem.

The advantage in liquid detergent formulation provided by the conjunct use of cation-exchange material in the wash portion of the home laundering cycle can be illustrated by consideration of the formulation of a presently sold liquid detergent composition.

TABLE V

	Percent
Linear sodium tridecylbenzene sulfonate -----	9
Linear sodium alkyl triethoxamer sulfate -----	6
Alkanolamides -----	2

Potassium pyrophosphate -----	15
Potassium xylene sulfonate -----	8
Optical brightener, color, suspending agents, perfume, impurities, etc. -----	3.5
Water -----	56.5

Of this formulation it is specified that one-half cup (or 140 grams) be used for a washing machine load comprising about 17 gallons of water. Since one mole of potassium pyrophosphate will complex just under one mole of calcium ions, the maximum hardness of water that could be completely softened by the specified amount of the above formulation is 100 p.p.m. Since it is not feasible to increase the potassium pyrophosphate content of the formula to more than about 20% without seriously reducing the amount of organic detergent, water of hardness greater than 150 p.p.m. will not be adequately softened. Therefore, the use of a cation-exchange material in conjunction with the detergent formulation as presently made will provide additional softening capacity for water of greater hardness and/or additional softening capacity for the rinses. Alternatively, part or all of the pyrophosphate could be eliminated from the detergent formulation (as well as the potassium xylenesulfonate which is present as a solubilizing or hydrotropic agent) and water softening achieved largely or solely by the adjunct cation-exchange material thus permitting a greater concentration of organic detergent to be incorporated in the detergent formulation should that be regarded as desirable; for example, the use of more compact packaging for equal effectiveness of product.

Similarly the concentration of detergency builder can be reduced when the solid detergent formulation is used in conjunction with cation-exchange material in the wash portion of the home-laundering cycle. It is present practice to prepare "built" laundry detergents with a minimum of inorganic builder, such as pentasodium tripolyphosphate (NaTPP), of 25 percent and as much as 50 percent. When the cation-exchange material is used as provided in the present invention the TPP can be reduced or even eliminated.

Those skilled in the art will recognize that the foregoing is a description of the use of an adjunct in the wash and/or rinse portions of the home-laundering cycle. Hence, the present invention provides a method of home-laundering in which the amount of soiled cloth washed at one time does not exceed about twelve to fifteen pounds and the volume of water employed in any portion of the cycle does not exceed about 17 gallons, wherein the water employed, at least in the wash portions of the laundering cycle, is contacted with an amount of cation-exchange material effective to reduce the concentration of calcium in and, preferably, to remove substantially all of the calcium from the water employed. It is presently preferred to make the cation-exchange material available to the home-launderer in a unit requiring regeneration after use in a single laundering when using water of maximum hardness and at less frequent intervals when using water of less than said maximum hardness.

What is claimed is:

1. In the method of home-laundering wherein in a wash step soiled fabric is contacted with water containing a detergent, wherein the washed fabric is separated from the water and in at least one rinse step of the laundering cycle the washed fabric is contacted with water free from detergent, and in a final step of the laundering cycle the rinsed fabric is separated from the rinse water, the improvement which comprises carrying out at least the wash step in the presence of a water-insoluble cation-exchange phosphorylated cellulose material containing about 5.3% phosphorus.

2. In a method as defined in claim 1 the improvement wherein the cation exchange material is phosphorylated cotton.

3. In a method as defined in claim 2 the improvement

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wherein the phosphorylated cotton has a calcium binding capacity of 30 milligrams of calcium per gram of cation exchange material.

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