Patented Mar. 9, 1948 2,437,253

UNITED STATES PATENT OFFICE

2,437,253

DETERGENT COMPOSITION

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No Drawing. Application January 8, 1940, Serial No. 312,842

4 Claims. (Cl. 252—109)

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Our invention relates to detergent compositions of matter and methods for improving and increasing the effectiveness of detergents.

The term "detergent" is employed generically in a sense to include any compound or composition having a cleaning action. By the term we intend to include more specifically the usual soluble soaps of fatty acids in all the forms and compositions and the so-called non-soaps, such as the sulfoderivatives of higher fatty compounds. With regard to the latter, we also use the term generically without distinction as to whether the most efficacious action is obtained in an alkaline or an acid medium.

Hardness in water has previously been considered an undesirable characteristic, particularly when the water is to be used with the soap type of detergents in washing or cleaning. The literature and the patents contain many disclosures pertaining to the treatment of hard waters for the purpose of eliminating, or at least minimizing, the undesirable results when used with detergents.

The hardness of water comprises salts of alkaline earth metals, such as calcium and magnesium, and other metals, such as iron. These may be rendered innocuous by taking them out of solution in the form of an insoluble precipitate. This is a cumbersome method and involves a separate operation and extensive equipment. They may also be rendered innocuous by "sequestering" the hardness, in which case it is converted into a component which does not yield calcium ions in sufficient concentration to react to form a soap precipitate. This, however, requires a relatively large amount of the sequestering compound.

Another approach to the problem of hardness in water has been to modify the detergent chemically so that it becomes relatively unaffected by the hardness of water in which it may be used. An example of such compositions would be the so-called "non-soap" detergents, such as the sulfated higher fatty alcohol or higher fatty amide types which are substantially insensitive to hardness. These compounds in most instances and unless used in combination with other ingredients, are relatively not as effective in detergent action as ordinary soap.

We have found, however, contrary to the prior conceptions of the necessity and desirability for removing the hardness or at least minimizing its effect upon detergents, that hardness can be utilized under controlled conditions to materially increase the effectiveness of detergents. In fact we have found that with a soft water or one of reduced hardness, it may be desirable to provide a controlled hardness in order to obtain an improved cleansing effect from a given detergent.

It is an object of our invention, therefore, to provide a method for increasing the effectiveness of detergents.

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It is a further object of our invention to provide a composition intended primarily for use as a detergent which will have an improved cleansing action in the presence of water.

We have found that the tendency of the soil particles, such as oleaginous and inert solid particles, to disperse and remain suspended in the wash water may be increased by providing a proportion of relatively insoluble colloidal-like particles. The effect preferably is accomplished if there is present a substance having such a high negative valency as to maintain the particles in a state of dispersion.

We have found as a result that the cleansing properties of a given detergent may be materially increased. A maximum removal of soil is obtained when the wash water containing the dispersion is removed from the article being cleansed. Likewise, as a result of our discovery the tendency for the soil to re-form or settle on the cleansed article is minimized.

The detergents, soaps, for example, act to emulsify the oily materials and deflocculate the solid or dirt particles. The soil must remain suspended or dispersed in the wash water so as to be removed with it rather than remain or be redeposited on the article to be cleansed.

The stability of an emulsion or suspension is dependent upon the negative potential carried by the dispersed particles and any condition tending to increase the dispersing potential tends to reduce the possibility of agglomeration or flocculation.

The colloidal particles which we propose to use in controlled amounts in accordance with our invention are maintained in a highly dispersed condition by providing them with a high negative potential by the addition of components of relatively high negative valency. Thus, nucleating points are provided for the soil which in turn acquires a negative dispersing charge, probably either by wetting as with an oil particle or by a surface adsorption as with a dirt particle. The negative potential nucleating points materially assist the action of the detergent by dispersing the soil and stabilizing the dispersion to permit removal with the wash water.

In the preferred embodiment of our invention, we control the formation of the insoluble colloidal particles to be dispersed by the addition of a suitable proportion of a compound capable of forming salts having a solubility less than that of the hardness normally present in water. Such compounds act to precipitate the hardness of water, for example, to provide the desired colloidal particles. Included in this class, for example, are sodium tetraphosphates, sodium polymetaphosphate, i. e., sodium hexametaphos-

phate, trisodium phosphate, tetrasodium pyrophosphate, or other alkaline metal phosphates, soap, calcium sensitive non-soap detergents, or other soluble materials which will precipitate hardness.

The colloidal particles formed with the hardness of water are then maintained in a dispersed condition by the presence in the water of an added substance capable of increasing the negative potential of the formed colloidal particles to such a degree that they remain suspended. Agents that may be employed most desirably because of their relatively high negative valency are alkali metal polymetaphosphates, tetrasodium pyrophosphates, and related compounds having a valency of 4 or more.

It will be apparent that in the case of tetrasodium pyrophosphates and similar high negative valency compounds which also exert a precipitating action on the hardness of the water, that only a single compound need be added to perform both functions.

It is important to observe that in utilizing substances of the type of tetrasodium pyrophosphate and sodium hexametaphosphate, for example, that only limited amounts may be utilized in practicing our invention for if amounts are added greater than that necessary to form a precipitate with the water hardness, that is to say a calcium salt of the phosphate, the desired colloidal precipitate will disappear and the calcium becomes "sequestered." It is well known that if a small amount of sodium hexametaphosphate or tetrasodium pyrophosphate, for example, are added to the hard water, a precipitate will be formed which may be sufficient to cloud the water. Upon addition of more of the phosphate, the original precipitate will redissolve and the water again becomes clear. The redissolving of the precipitate is the result of the formation of soluble complexes with the added phosphate which do not yield calcium ions in sufficient concentration to result in precipitation. For example, one anion of tetrasodium pyrophosphate is necessary to precipitate two cations of calcium hardness. One additional anion of tetrasodium pyrophosphate is necessary to form the complex with or sequester the calcium pyrophosphate.

The usefulness of the pyro- and hexametaphosphates, for example, in connection with soap is ordinarily ascribed to this action of, in effect, removing the calcium ions from solution by sequestering them and thus preventing the formation of insoluble calcium soaps. It has previously been considered as necessary and desirable in washing that sufficient of the phosphate be added to avoid the cloudy effect and redissolve or sequester the calcium. In accordance with our invention we prefer the conditions in which the water may be cloudy for such condition is evidence of a fine colloidal precipitate which we have found can be utilized to increase the effectiveness of detergents. Thus, preferably only such small amounts of the water hardness precipitating agent of the "sequestering" type should be added as to form the precipitate. Subsequent "sequestering" should be minimized in order to obtain the maximum effect desired in accordance with our invention.

A careful control of the amount of such precipitating agent to be added is particularly necessary if the "sequestering" type of agent is also to be utilized as the colloidal dispersing agent because of its high negative valency. For this reason, in utilizing substances of the type of hexametaphosphates or tetrasodium pyrophosphates, it is desirable only to add the minimum amount which will furnish the necessary colloidal dispersion so that any additional amount of the phosphate added will be effective to disperse the colloidal particles by increasing their negative potential without material "sequestering" or redissolving.

Our invention and the result obtained is independent of the alkalinity of the added ingredient. For example, when a non-soap detergent is used which is more effective in an acid solution, and an alkaline high negative valency compound is used, there may also be added an acid salt. This will usually be done only in the case of certain non-soap detergents. When our invention is used with soap as the detergent, and a relatively highly alkaline negative valent compound, such as tetrasodium pyrophosphate is used, the alkalinity need not be, and preferably is not, decreased. The amount used may be so small as to make it unnecessary to modify or correct the resulting or normal alkalinity of the wash water.

It is possible to utilize our invention with detergents which have a tendency to react with the hardness of water forming insoluble compounds, such as soluble salts of fatty acids which form calcium soaps or non-soap detergents that are sensitive to water hardness. For example, when ordinary soap is used with hard water, the calcium soap precipitate formed may be employed with advantage to obtain an improved detergency in accordance with our invention. Such precipitates may be used with the colloidal precipitates formed by the other addition agents. In such cases the proportions of high negative valency dispersing agents could desirably be so adjusted as to act to disperse any such calcium or magnesium soaps present in addition to other precipitated hardness.

One of the properties heretofore considered particularly desirable in the so-called "non-soap" detergents has been their insensitiveness to the hardness in water. That is, they do not react to form, for example, insoluble calcium compounds as do the soluble salts of fatty acids. As a result, certain non-soap detergents have been used in considerable quantities in districts known to have water of an undesirable hardness. By the use of the so-called "non-soap" detergents, it has been possible in the hard water districts to wash without the formation of the well-known scum (calcium soaps) which is characteristically formed when ordinary soaps are used.

We have found, however, that although the resistance to hardness may be one of the desirable features in a detergent, yet the detergent effectiveness may be less than that desired as a result of this characteristic. We have found that the effectiveness of the non-soap detergents can be increased by providing in the wash water nucleating points for the soil, comprising colloidally dispersed particles along with an ingredient for supplying high negative potentials, as already pointed out.

This may be accomplished in several ways. It has been found desirable to increase the sensitiveness of the non-soap detergents to water hardness by means of which insoluble calcium salts, for example, of the non-soap detergents are formed as with soap. The precipitate is maintained in a dispersed condition by the added material of high negative potential as described above, and thus provides nucleating points for

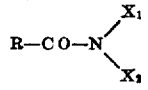
the soil. The soil dispersing action and detergent effectiveness are thereby improved.

As an alternative or complementary procedure, non-soap detergents may be utilized having a reduced solubility. In such case, although they might not react with the hardness to form insoluble particles, yet their reduced solubility would cause them to become absorbed by the soil particles, thus giving to such particles a negative potential. The potential thus acquired tends to hold the soil particles in a dispersed condition facilitating removal with the wash water.

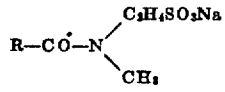
Compounds of the type obtained by condensing a higher fatty acid with the alkaline metal salt of a hydroxy alkane sulfonic acid, such as myristic oxyethane, are believed to be compounds of the latter type and are highly desirable in utilizing the water hardness to increase the detergent effect.

Certain of the salts of the sulfonated straight chain alcohols, sometimes referred to as the "gardinols," and some of the "santomerse" compounds, such as the alkyl-substituted aromatic sulfonates, as for example, dodecyl benzene sodium sulfonate, appear to form relatively insoluble calcium salts, for example, and thus may be utilized in the formation of dispersed nucleating points in accordance with our invention.

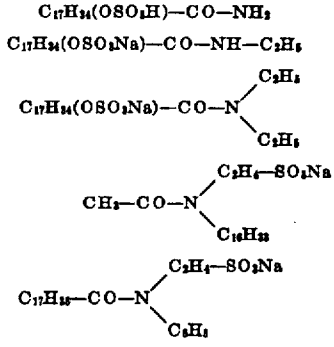
Such compounds of low solubility may be desirably combined with the higher fatty acid amides having the formula



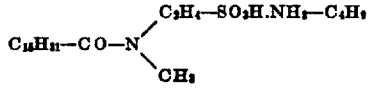
in which R is an aliphatic, an aliphatic-aromatic, or a cyclo-aliphatic radical, in which X_1 is hydrogen or a radical denoted by R, and in which X_2 is hydrogen or a radical denoted by R, said compound having a total number of carbon atoms of at least 8 and containing at least one sulfonic or sulfonic acid group the hydrogen of which may or may not have been replaced by a metal to form a corresponding sulfate or sulfonate group. Examples of such compounds are the alkyl taurides, such as



Additional examples of this general type are as follows:



and



In the same connection it probably is desirable to use the higher fatty acid taurides having at least 14 to 16 carbon atoms or more in order to reduce their solubility. Desirable combinations of these detergent ingredients are disclosed in our copending application Serial No. 253,020, filed January 26, 1939, now Patent No. 2,279,314, issued April 14, 1942.

It will be noted as a result of our invention that the normal hardness of water formerly considered detrimental is utilized and made highly desirable for the purpose of increasing effectiveness of a detergent of either the soap or non-soap type for cleaning purposes. Water hardness varies considerably between districts, but we have found that an ordinary hard water will average about 300 parts per million and formulas may be adjusted utilizing such hardness as a standard or may be adjusted to the hardness of water in a selected district.

If the natural water hardness is not believed to be sufficient to form the desired dispersion of colloidal particles, a hardness, so-called, may be included in the detergent composition which will react with the detergent or ingredient of high negative valence, such as tetrasodium pyrophosphate or both, to form a precipitate suitable to be dispersed by an added substance of a high negative valency and thus become available for nucleating points. It may even be found desirable in all cases to include such a hardness substance in the desired commercial formula in order to assure its presence. Calcium sulfate, calcium chloride, calcium acetate, calcium nitrate or other water soluble calcium, magnesium or iron salts may be utilized for this purpose. However, with regard to the magnesium and iron salts, care would have to be taken to avoid possible undesirable secondary effects. With detergents which are sensitive to calcium hardness, such as soap and a certain few non-soap detergents, care also desirably must be taken not to have present in the composition such amounts of hardness as to form an excessive amount of precipitate, but rather to have only such amounts present as will form a precipitate and in such an amount as can be maintained in a dispersed condition by the imposed electric charge from the added substance having the high negative valency.

It will now be appreciated that in accordance with our invention many detergents are more effective in hard waters than in soft. It can also be appreciated that as a result of the practice of our invention, it is now possible to obtain a detergency with both soaps and non-soaps in soft waters, that is, waters free from hardness, which will be the equivalent of waters containing a substantial hardness.

As already pointed out, it has long been known that calcium ions may be precipitated from non-acid solutions by the additions of a small amount of substances such as tetrasodium pyrophosphate and that the precipitate of the calcium pyrophosphate may be redissolved by an excess of tetrasodium pyrophosphate over that necessary to form the precipitate.

We have demonstrated by a photoelectric means, which translates the amount of precipitate into a galvanometer deflection, that the additions of very small amounts of tetrasodium pyrophosphate to water having a calcium hardness of 750 parts per million results in a rapidly increasing precipitation up to an over-all con-

centration of about 0.1% of the pyrophosphate. Additional amounts of tetrasodium pyrosphosphate then were found to bring about a gradual re-solution of the precipitate until at an over-all concentration of about 0.55% tetrasodium pyrophosphate re-solution of the calcium pyrophosphate precipitate is substantially complete. Only the phosphate was added to the water in order to avoid any clouding effect which would tend to minimize the sensitivity of the galvanometer.

With a water hardness of about 300 parts per million, it has been found, utilizing the same technique, that a maximum precipitation of calcium pyrophosphate occurs at concentrations of about 0.04% tetrasodium pyrophosphate with a substantially complete re-solution of the calcium pyrophosphate at about 0.09%.

The phenomena of precipitating the calcium salts with a phosphate, for example, while avoiding any substantial subsequent sequestering of them may be utilized to advantage with detergents including the soap and non-soap types. It has been found that substantially less than 10% of tetrasodium pyrophosphate, for example, based upon the weight of a soap permits the desired formation and utilization of precipitated colloidal particles as dispersed nucleating points in the presence of a soap in ordinary concentrations and with water of average hardness.

Other such precipitating substances would be used in relatively proportional amounts with detergents. In some instances, only a portion of the available hardness need be precipitated as the colloidal-type particles to secure the desired effective detergent action. Also, as already pointed out, a part of the hardness may be precipitated by soap or a non-soap detergent if the latter is calcium sensitive. In either event, less precipitating agent of the phosphate type may be used than would be otherwise necessary.

In a composition comprising 65% of soap and 35% of other ingredients, it has been found that a maximum detergent effectiveness is obtained with tetrasodium pyrophosphate in amounts of 2½% based upon the weight of the soap composition. In some cases, depending on the hardness of the water, and the amount of soap employed in a given washing operation, 5% or 8% of tetrasodium pyrophosphate may be preferred. Suitable adjustment of the composition may be made based upon the relationship between the tetrasodium pyrophosphate and other equivalent phosphates used.

In connection with non-soap detergents, we have found that amounts of tetrasodium pyrophosphate of between about 10% and 50% or more based upon the weight of the detergent, may be used, having in mind the object of obtaining a desirable and effective colloidal-type precipitate of the hardness, so as to increase detergency. The amount to be used will depend in general upon factors similar to those involved with soap. However, it should be noted that with regard to non-soap types of detergents, smaller amounts of such detergents will be used because of their greater detergency effectiveness. Thus, the amount of detergent available as a hardness precipitating agent is less. Also, the non-soap detergents usually are less effective as precipitating agents. Both of these factors call for a greater proportion of the pyrophosphate type of addition agent in order to obtain the necessary precipitate of nucleating points. By way of illustration, the amount of pyrophosphate in a standard formula of a non-soap detergent may

be at least five times the amount in a standard soap formula.

If an added agent of the type of tetrasodium pyrophosphate is used with a detergent composition containing soap, it would not be necessary to have more of such added agent present than the amount of soap necessary to precipitate the hardness of the water for we have found that the soap would act to precipitate the hardness first thus making such added agent available to disperse the precipitate by imposing upon it a negative potential.

In general, the amount of tetrasodium pyrophosphate, for example, which would be sufficient to precipitate the hardness of a water of average hardness would also be sufficient to maintain the precipitate dispersed in a relatively permanent suspension, and so improve the detergent effectiveness of the composition. In using added agents with a high negative potential of the type of tetrasodium pyrophosphate, however, it should be kept in mind that although larger amounts might be added, that redissolving or sequestering of the precipitate should be avoided for to do so would diminish the available nucleating points which act to increase the detergent action. The dispersion brought about by the high negative potential agent acting upon the precipitate should at least be sufficient to permit removal of the soil and dirt in a suspended condition upon separation of the wash water.

In compositions containing non-soap detergents of a type relatively ineffective as hardness precipitating agents, a sufficient amount of a high negative potential dispersing agent must also be added to obtain and maintain the desired dispersion of the colloidal-like particles. If hardness of the water is precipitated with the same agent as is used to obtain the dispersion, the amount added must be such as to form the precipitate and still have sufficient present to disperse it. In general, with substances of the type of tetrasodium pyrophosphate, an amount approximately equivalent to the amount of precipitating agent would be sufficient to obtain the desired dispersion.

In general, with regard to detergent compositions of either the soap or non-soap type, the amount of added dispersing agent can be adjusted most effectively if it is also effective as a colloidal dispersing agent even though it may have the property of redissolving the precipitate when used in excess. Of this type of added agent, tetrasodium pyrophosphate appears to be the most desirable. The negative valency of this substance is 4. Other salts having a similar or higher negative valency may be used if desired with suitable adjustment of the proportions dependent upon their precipitating and dispersing characteristics relative to tetrasodium pyrophosphate.

We have been able to demonstrate by machine and hand washing tests made on wool, silk, rayon, and cotton standard soiled cloths, as well as in standard dishwashing tests, that the detergent effectiveness of a soap composition, for example, is materially increased, if substances of the type of tetrasodium pyrophosphate are added to the soap or soap solution in amounts as low as 5% and substantially less than 10% based on the weight of the soap composition. Washing tests have been run employing amounts of soap that would give equal amounts of suds. Also, tests have been run employing amounts of soap having

equal weights of fatty acids. Relatively soft water was used in one series of tests and a water of approximately standard average hardness of 300 parts per million used in another series.

Soap compositions, at least of the spray-dried type, used in laundering and dishwashing are normally used in concentrations between .2% and .5%, particularly in laundering, although greater concentrations, as much as 1¼% to 1½%, may be used in dishwashing.

The cloth washing tests, for example, have shown that the addition of tetrasodium pyrophosphate in the amount of 5% to a soap composition gives a material increase in detergency as compared with a similar composition but without the tetrasodium pyrophosphate. These tests demonstrate, however, that the addition of further increased amounts of tetrasodium pyrophosphate do not give any appreciable increase in detergency, but unexpectedly, 10% of tetrasodium pyrophosphate with a similar composition brings about a decrease in the detergent effect.

These washing tests have also demonstrated that there is an increase in detergent efficiency when similar compositions are used with hard water as compared with soft water, indicating the advantage of operating under conditions where there is controlled dispersion of suspensoids, obtained by precipitating the water hardness and dispersing it in accordance with our invention.

The amount of so-called added hardness, that is, material available in the composition to form a precipitate of a colloidal nature, which can be maintained suspended, is, in general, related to the hardness of the wash water with which it is to be used and act only to replace or supplement the natural hardness. It will be appreciated, therefore, that the amount to be added would in no case be greater than that found desirable for providing the greatest increase in detergent efficiency, and would probably not be greater than the equivalent of a water hardness of three hundred parts per million. In view of the fact that most waters available in metropolitan districts already contain a natural hardness, the amount of so-called artificial hardness, for example, calcium sulfate, to be added would be the minimum amount which would provide an improved detergent effect.

Preferred examples of our soap composition in accordance with our invention are as follows:

	Per cent
A. Soap, anhydrous	62
Sodium silicate	8
Soda ash	7
Tetrasodium pyrophosphate	8
Salt, etc	1
Water	14
B. Soap, anhydrous	65
Sodium silicate	10
Soda ash	3
Tetrasodium pyrophosphate	5
Salt, etc	1
Water	16
C. Soap, anhydrous	65.5
Sodium silicate	14.0
Soda ash	1.0
Hexametaphosphate	2.5
Salt, etc	1.0
Water	16.0

Preferred examples of a non-soap composition embodying our invention are as follows:

	Per cent
D. Myristic methyltauride	10
Palmitic methyltauride	10
Tetrasodium pyrophosphate	20
Sodium sulphate	39
Calcium sulphate	10
Salt, etc	6
Starch	5
E. Myristic methyltauride	10
Palmitic oxyethane	10
Tetrasodium pyrophosphate	18
Sodium bisulphate	9
Sodium sulphate	42
Salt, etc	6
Starch	5
F. Stearic methyltauride	5
Myristic methyltauride	10
Palmitic oxyethane	15
Disodium-dihydrogen-pyrophosphate	12
Sodium sulphate	49
Salt, etc	9

Variations within limits, dependent upon equivalency and relative effectiveness, may be made in the ingredients employed and in their proportions without departing from our invention and all such variations are to be included in our invention as defined in the claims. While we have set forth certain explanations for the improved results obtained as the result of the practice of our invention, it should be appreciated that some elements of any explanation may be theoretical in nature. As a result, we do not wish to be limited to the particular theory or explanation explaining the improved results obtained. Other theories or explanations than those disclosed may be developed which will satisfactorily explain the desired results. Our invention is directed to the improved detergents disclosed and claimed herein and the methods for improving the detergency of soap and non-soap detergents as described herein and claimed.

We claim:

1. In a process of removing soil from an article by washing with water, the steps comprising adding to said water a water soluble alkaline earth compound to impart a hardness of approximately the equivalent of 300 parts per million to said water, adding a water-soluble compound that forms a water-insoluble precipitate with the alkaline earth compound, and maintaining said precipitate in an insoluble but dispersed condition by the presence in said solution of a water soluble phosphate having a negative valency of at least 4.

2. A detergent composition capable of improved effectiveness when used in hard water, comprising soap, a water-soluble alkaline earth compound in an amount to form a hardness in the water of approximately the equivalent of three hundred parts per million when said composition is used in the amount ordinarily employed in a detergent operation, and a water-soluble phosphate having a negative valency of at least 4 in an amount to disperse the precipitate resulting from the addition of said composition to said hard water but insufficient to sequester said precipitate when the composition is employed in said amount ordinarily used in a detergent operation.

3. In a process of removing soil from an article by washing in hard water, the steps comprising introducing a finely divided precipitate into said

water by adding soap and a water-soluble chemical capable of reacting with the hardness in the said water to form a precipitate, and maintaining said precipitate in an insoluble but dispersed condition by the presence in said water of a water-soluble phosphate having a negative valency of at least 4.

4. In a process of removing soil from an article by washing in hard water, the steps comprising introducing a finely divided precipitate into said water by adding soap and a water-soluble chemical capable of reacting with the hardness in the said water to form a precipitate, and maintaining said precipitate in an insoluble but dispersed condition by the presence in said water of about 2½% to 8% of tetrasodium pyrophosphate based on the weight of said soap.

LLOYD F. HENDERSON.
BERNARD L. MAXWELL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,092,913	Fiske	Sept. 14, 1937
2,093,927	Preston	Sept. 21, 1937
2,159,381	Jochum et al.	May 23, 1939

FOREIGN PATENTS

Number	Country	Date
198,681	Great Britain	Aug. 7, 1924
253,554	Great Britain	Sept. 24, 1927
364,565	Great Britain	Dec. 30, 1931
431,682	Great Britain	July 8, 1935
435,475	Great Britain	Sept. 23, 1935
443,731	Great Britain	Mar. 2, 1936
447,072	Great Britain	May 12, 1936
452,649	Great Britain	Aug. 24, 1936
461,328	Great Britain	Feb. 15, 1937

OTHER REFERENCES

Soap, November 1938; pages 24–26 and 26A.
Ibid., January 1939; pages 24–26 and 69.

Certificate of Correction

Patent No. 2,437,253. March 9, 1948.

LLOYD F. HENDERSON ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 12, list of references cited, under the heading "UNITED STATES PATENTS" insert the following:

1,746,170	Ullman	Feb. 4, 1930
1,870,318	Stoddard	Aug. 9, 1932

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of May, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

water by adding soap and a water-soluble chemical capable of reacting with the hardness in the said water to form a precipitate, and maintaining said precipitate in an insoluble but dispersed condition by the presence in said water of a water-soluble phosphate having a negative valency of at least 4.

4. In a process of removing soil from an article by washing in hard water, the steps comprising introducing a finely divided precipitate into said water by adding soap and a water-soluble chemical capable of reacting with the hardness in the said water to form a precipitate, and maintaining said precipitate in an insoluble but dispersed condition by the presence in said water of about 2½% to 8% of tetrasodium pyrophosphate based on the weight of said soap.

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