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DETERGENT BRIQUETTE

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This invention relates to an improved briquetted detergent compound and includes a novel process whereby the product may with advantage be produced.

The briquette of my present invention is unique in its combination of detergent characteristics and other physical and chemical properties which make it highly satisfactory for use in modern mechanical washing operations.

Modern mechanical methods and apparatus for washing dishes, milk cans and the like, particularly where the operation is continuous or prolonged, have presented the serious problem of maintaining an alkali concentration in the wash tanks between desirable and restricted limits. Commercial experience has shown that this may be accomplished in a dependable and virtually automatic manner by dissolving alkaline briquettes in suitable auxiliary equipment and dispensing the resulting solution into the wash tanks at a predetermined rate. A very considerable amount of research has been carried out in view of developing detergents having chemical and physical characteristics satisfactory for this purpose.

The problem presented involves not merely the production of a material or mixtures of materials having the desired detergent characteristics but also the development of a product which, in addition to meeting that requirement, can be economically produced in the desired physical form possessing other essential physical characteristics.

For instance, it is desirable that the detergent be in briquette form; that the briquettes be sufficiently hard and strong to withstand ordinary handling; be chemically and physically stable and non-deliquescent so as to withstand storage and the necessary handling and of such structure as will not disintegrate under the conditions of use.

Inasmuch as the control of the rate at which the alkali is dispensed into the washing operation largely depends upon the dissolving rate of the briquette, it is desirable that the briquette not only have a satisfactory degree of uniformity in its composition but also that it have a uniform solubility rate.

It is, of course, also essential that the composition of the cleansing solution be such as to avoid harmfully affecting the material being washed either by attacking the material or by forming deposits or coatings thereon. It is further essential that the composition of the detergent be such as to avoid deleteriously affecting

the parts of the mechanical washer and the deposition of scale in the various chambers thereof.

It has been proposed to produce detergent briquettes for such use by fusing the detergent or detergent mixture and casting the fused material by drawing it off into molds to cool. For example, briquettes have been produced by fusing mixtures of trisodium phosphate and soda ash. However, the relatively high temperatures required to fuse the detergent or detergent mixtures have been a decided handicap in the production of satisfactory detergent briquettes, as many substances, the presence of which is highly desirable in detergent mixtures, are driven off or decomposed at temperatures below their fusion point or at temperatures necessary for fusing other desirable constituents.

This temperature requirement has not permitted the incorporation in detergent mixtures so produced of many very effective water conditioners and surface active agents such as synthetic detergent and wetting agents. Consequently, the use of such fused detergent briquettes has not been wholly satisfactory. For instance, particularly under adverse water conditions, their use has resulted in the precipitation of natural hardness of the water supply and the tendency to form scale on the inner surfaces of the mechanical washers with which the detergent is used. Rapidity of this scale formation depends upon the degree and nature of the hardness of the water and, in general, increases with the concentration of hardness of the water supply. If not periodically removed, this scale interferes with the normal functioning of the equipment. Further, this precipitated hardness interferes to a greater or less extent with the cleansing operation.

The presence of a water conditioner such as tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) in the alkaline solution tanks of the mechanical washers has been found to inhibit or greatly retard scale formation. Also, the addition of surface active agents has been found further to enhance the cleansing action and to afford improved rinsing. However, for the reasons stated above, the incorporation of these materials in fused anhydrous detergent briquettes has been impractical.

Detergents have heretofore been produced in block form by crystallization or solidification of the detergent or detergent mixtures from aqueous solutions; for instance, by the evaporation of water therefrom or by causing a chemical or physical union of the water or a proportion there-

of with the detergent. The resulting blocks of detergent material have usually been reduced to a granular or powdered form before use.

It has also been proposed to use these detergent blocks as such in detergent operations. However, so far as I am aware, the detergent blocks so produced prior to my invention have fallen short of the requirements essential to their satisfactory commercial use in mechanical washing operations.

The detergent briquette of my present invention may be formed without resort to high temperatures and its constituents and proportions thereof may be varied over a considerable range to meet the requirements of the particular washing operations in which it is to be used. Further, the physical limitations and deficiencies common to previous detergent briquettes are overcome. My improved briquettes consist of a dense crystalline aggregate of relatively uniform composition. They are hard and strong and chemically and physically stable, being capable of withstanding the conditions of shipment and storage essential to ultimate commercial use without material deterioration, disintegration or deliquescence. They do not disintegrate under normal conditions of use and have a uniform solubility rate. Also, since they can be produced without resort to high temperatures, various desirable addition agents unstable at higher temperatures may be incorporated therein to meet special water conditions or detergent requirements. Accordingly, objectionable precipitations of natural hardness of the water used may be inhibited or greatly reduced and the detergent action of the resulting washing solution materially improved. Further, the congealing and hardening time of my briquettes during molding is sufficiently rapid to permit their economical commercial production.

The detergent mixture of which my improved briquettes are composed consists essentially of trisodium phosphate, sodium silicate, sodium carbonate and water. Advantageously, it may also contain tetrasodium pyrophosphate or a surface active agent or both. The presence of tetrasodium pyrophosphate is desirable because of its water conditioning properties but also I have found the use of controlled proportions of this pyrophosphate in my briquettes to improve their physical structure. As previously stated, the proportions of the several constituents may be varied over a considerable range, hereinafter specified, to meet specific detergent requirements without loss of the desirable physical or mechanical characteristics of the resultant briquette.

In the preparation of my briquettes, the trisodium phosphate may be introduced in the form of the ordinary commercial hydrated product generally represented by the formula $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Theoretically, this material contains 56.8% water. However, repeated analyses indicate that the water content of the trisodium phosphate which I have used in the development of my improved briquette is approximately 53%. Consequently, the proportions specified herein are based upon the latter figure. Trisodium phosphate, having a higher or lower water content, may be used, providing appropriate compensation be made for the different proportion of water contained therein. Also, materials which react under the process conditions to form trisodium phosphate, for instance disodium phosphate and caustic soda, may be substituted for an equivalent proportion of trisodium phosphate, appropriate allowance being

made for the water content of such reacting materials and water produced by the reaction.

The sodium silicate constituent of my briquettes should have an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of not less than 1 nor greater than 2. I have obtained excellent results by supplying the sodium silicate in the form of water glass of 41° Bé. gravity and consisting of 8.9% Na_2O , 28.7% SiO_2 and 62.4% water, and reacting the water glass with caustic soda in sufficient proportion to produce a sodium silicate of the desired $\text{Na}_2\text{O}:\text{SiO}_2$ ratio. Other water glass or sodium silicate in solid form may be used in accordance with my invention by making appropriate allowance for differences in composition. For example, instead of the use of water glass and sufficient caustic soda to react therewith to form the metasilicate, sodium metasilicate as such may be substituted wholly or in part for the water glass and caustic soda equivalent. When such substitution is made, due allowance should also be made for the amount of water which would otherwise be formed by the reaction between the water glass and caustic soda.

The caustic soda may be supplied in solid form such as the usual commercial grade of about 76% Na_2O . However, other forms of caustic soda, such as the commercially available 50% solution, may be substituted provided appropriate allowance is made for the difference in composition.

The sodium carbonate may conveniently be supplied as anhydrous soda ash and the proportions stated in the several formulae appearing herein are based upon the use thereof. However, it may be supplied in the form of hydrates such as mono or deca hydrates, appropriate allowance being made for differences in composition.

Similarly, the tetrasodium pyrophosphate may be supplied in the usual anhydrous form and proportions thereof appearing herein have reference to such material.

Before defining the range of proportions of the various ingredients incorporated in my improved briquettes, I shall describe my novel process of compounding and preparing the same.

The compounding of my improved detergent is advantageously carried out in a conventional steam-jacketed kettle equipped with a stirring device. I have obtained excellent results in preparing and in duplicating the composition and structure of the briquettes by adhering to the following procedure: The predetermined amounts of water glass, trisodium phosphate, caustic soda and additional water, if any is required, are placed in the kettle and heated with constant agitation until the mass is fluid. The temperature is then maintained at a maximum just beyond which substantial evolution of steam would occur with a resultant material loss in water content. Higher temperatures are to be avoided as it is desirable to reduce to a minimum the amount of water lost during the heating operation and to avoid decomposition of less stable ingredients. By minimizing the water loss the proportion of water in the product may be effectively controlled by regulation of the total amount of water added to the batch.

The maximum temperature to which the material is heated, and at which it is held, depends primarily upon the concentration of the solution in the fluid mass and is usually found to be within the range of about 90-110° C. The fluid mass is held at this temperature until the mass clarifies, advantageously until maximum clarity is obtained. This usually requires from 10 to 20 min-

utes, depending upon the composition and amount of solute.

After clarification of the mass the predetermined amount of soda ash is then added and thoroughly mixed with the fluid mass. If the addition of soda ash results in a decrease in temperature to a point at which the mass is too viscous for final pouring, the temperature may be increased until adequate fluidity is obtained, care being taken to avoid temperatures which would result in the material loss of water. It tetrasodium pyrophosphate is to be incorporated in the briquettes, it may be added and thoroughly mixed into the mass in the kettle at this point, or it may be found advisable to incorporate the pyrophosphate into the mass prior to the addition of the soda ash, particularly if the pyrophosphate is in a slowly soluble form.

The mixture is then drawn off into suitable molds and allowed to congeal until the briquettes have developed sufficient mechanical strength to permit their removal from the mold. The necessary molding time will generally vary from about 1 hour to several hours, depending upon the composition of the mixture. Where a sodium silicate other than water glass is used, it should be placed in the kettle at that stage of the operation where the water glass would have been introduced.

On cooling, detergent compositions of this type seem to expand somewhat and this, combined with their tendency to adhere to metal surfaces of the molds, has previously presented considerable difficulty in the molding of detergent materials. I have found that, by using flexible briquette molds, such as molds made of rubber or similar materials, these difficulties are eliminated.

Where it is desirable to incorporate in the briquettes a so-called surface active agent, such material may be introduced into the mixture just prior to withdrawal from the kettle. However, where such addition agent is in solid form and has a relatively slow rate of solubility, I prefer to add it prior to the addition of the soda ash. Various surface active agents capable of withstanding the necessary processing temperatures in an alkaline environment may be so incorporated in my briquettes to meet special conditions encountered in specific detergent operations for which the briquettes are intended; for example, a product consisting principally of sodium lauryl sulfate, marketed under the trade-name "Orvus" or one consisting principally of sodium dodecyl benzene sulfonate, marketed under the trade-name "Nacconol," each of which I have used to advantage.

The addition of even a fraction of 1% of many of the so-called surface active agents or synthetic detergent or wetting agents has been found materially to reduce the dissolving rate of the resulting briquette. This effect has been found to increase generally as the amount of the agent is increased. Also, under similar conditions of preparation, the addition of many of these surface active agents somewhat increases the molding time. Though, for some purposes, a reduced dissolving rate is undesirable, the addition of a predetermined amount of a surface active agent is of value in controlling the dissolving rate to meet a specific requirement in this respect. The primary purpose of the addition of these surface active agents is to increase the wetting power of the washing solution and so tend to improve the detergent and rinsing properties thereof. The addition of many of these materials in proportions as small as 0.1% has a noticeable effect.

One of the advantages of my invention is that such surface active agents may be incorporated in my briquettes, if desirable, either for controlling the dissolving rate or for increasing the wetting power of the washing solution. However, under many conditions encountered, the detergent mixture need not be so supplemented.

While the proportions of the various ingredients used may be varied over a considerable range without destroying the desirable physical or mechanical properties of the resulting briquette, I have found the permissible range of variation to be rather sharply defined. An increase in the proportion of trisodium phosphate with a corresponding decrease in soda ash, other conditions being the same, tends to decrease the congealing or molding time of the resultant briquette. However, I have found that the proportion of anhydrous trisodium phosphate in the resulting briquette cannot much exceed 15% by weight without detrimentally affecting the structure of the briquette. This is first evidenced by a tendency for the briquette to develop checks or cracks a day or so after the briquette has been molded. As the trisodium phosphate content is further increased, the congealed mass cracks and otherwise decrepitates to an extent that prevents removal of the briquette intact from the mold. Generally, when the proportion of trisodium phosphate approaches this upper limit of the range for that ingredient, i. e., about 15% by weight, the silicate content should approach its lower limit in order to obtain the most satisfactory conditions with respect to molding time and structure of the briquette.

Where the proportion of anhydrous trisodium phosphate in the finished product is less than about 1% by weight, I have found the briquettes to be so slow in congealing that the molding time is excessive. Further, the proportion of sodium silicate which can be employed without detrimentally affecting the physical structure of the briquette is limited where less than about 1% by weight of anhydrous trisodium phosphate is present.

I have found the desirable proportions of anhydrous sodium silicate in the finished product to be within the range of about 1% to about 22% by weight. As the proportion of anhydrous sodium silicate exceeds this maximum, the molding time increases toward an impracticable amount and above an anhydrous silicate content of about 25% briquetting difficulties are encountered. With less than about 1% anhydrous sodium silicate present, the physical characteristics of the briquette are impaired.

Where water glass, such as previously described, or other sodium silicates having a ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ less than 1 are used, I add caustic soda in proportions sufficient to combine with the water glass to form the metasilicate, in which the ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ is unity, but not in excess of that required to form the orthosilicate in which the ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ is 2. In general, best results are obtained where the proportion of caustic soda so employed is within the range required to produce a mixture of metasilicate and orthosilicate in proportions of from 1 to 2 to 2 to 1. However, satisfactory results may be obtained with the proportion of anhydrous sodium silicate constituent within the range of about 1% to about 22% whether it be the metasilicate, the orthosilicate or a combination of the two, including a silicate having a molar $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of $1\frac{1}{2}:1$ which may be desig-

nated sesquisilicate. This maximum may be increased to about 25% but, particularly where the silicate constituent is the orthosilicate, less desirable physical structures and molding characteristics are obtained when such larger proportions of silicate are used.

Where the proportion of the sodium silicate constituent is in the extreme upper portion of the range, I have found the molding time to be reduced when the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio does not much exceed unity. Further, when the proportion of the sodium silicate constituent is about in the middle of the prescribed range, the molding characteristics, and to some extent the structural characteristics, are frequently improved by adjusting the alkalinity of the sodium silicate constituents to approximate that of the sesquisilicate.

The amount of water present in the detergent composition is of major importance both with respect to molding time and mechanical structure of the resultant briquette and also its detergent content. It is essential that sufficient water be present during the processing to produce under processing conditions a mass sufficiently fluid to permit satisfactory mixing and pouring into the molds and have satisfactory molding characteristics. However, the addition of an excess of water is to be avoided since the processing preferably does not involve conditions under which excess water would be eliminated.

I have found the permissible range of proportions of water in my briquetted product to be from about 30% to about 40% by weight. It is necessary that the product contain sufficient water to permit satisfactory pouring and molding but an increased amount of water in the product results in a corresponding reduction in the alkali content of the briquette. The proportion of water present also has a distinct effect upon the physical characteristics of the briquette. Generally, proportions of water as high as 40% do not unduly prolong the congealing time or materially impair the physical structure of the briquette. However, proportions of water in excess of about 40% have been found to increase the molding time to impracticability and to affect adversely uniformity of structure of the resulting briquette. When the water content much exceeds this upper limit, there is a tendency toward segregation during the congealing period.

The optimum amount of water present in the finished product appears to depend to a considerable extent upon the proportion of other ingredients present. Usually more satisfactory results are obtained where the proportion of water is not much in excess of that required to give sufficient fluidity for pouring.

In determining the quantity of water, if any, to be added as such in the compounding operation, due consideration must be given to the amount of water present in the various constituents either as water of crystallization or otherwise and of water formed by chemical reactions. A small amount of water may be vaporized or lost during the compounding of the detergent mixture, particularly if the higher temperature be used. The amount of water thus lost is usually of no particular consequence. However, if the amount of water thus lost is excessive, additional water may be added to the batch.

Where tetrasodium pyrophosphate is to be incorporated in my briquettes, I have found proportions of about 15% by weight usually to be

sufficient for most water conditions. However, an amount in excess of 15% may be incorporated, if desirable, without destroying the physical structure of the resultant briquette.

When the proportions of anhydrous trisodium phosphate or of anhydrous sodium silicate are in the upper end of the respective ranges, the molding and structural characteristics of the briquettes are noticeably improved by the addition of tetrasodium pyrophosphate.

When the proportion of sodium silicate approaches the extreme upper limit, particularly when the alkalinity of the silicate approximates that of orthosilicate, proportions of pyrophosphate in excess of 15% may be added with advantage.

Where the pyrophosphate is added in proportions approximating 15%, the maximum permissible proportion of trisodium phosphate may be extended somewhat above 15%. For this purpose, proportions of the pyrophosphate in excess of 15% may be added with advantage, for example 20% to 25%.

When the proportion of anhydrous sodium silicate is at about the middle of the prescribed range for that constituent, and particularly when the alkalinity of the silicate constituent approaches that of sodium sesquisilicate, the proportion of tetrasodium pyrophosphate may be varied throughout the stated range without materially benefiting the physical structure of the resultant briquette. Where the proportion of the soda ash constituent approaches the upper limit of the prescribed range and the proportions of the trisodium phosphate and the sodium silicate constituents are each in the lower portion of their respective ranges, the molding and structural characteristics of the briquette are improved by the addition of tetrasodium pyrophosphate.

Where the addition of a water conditioner is required, a minimum proportion of about 2% to 3% is usually desirable. However, in accordance with this invention, any effective minimum may be used or, if desired, this material may be entirely omitted.

Though sodium carbonate is an essential constituent of my briquetted product, the proportions of sodium carbonate present do not appear to be particularly critical. The range of variation is usually from about 20% to about 50% by weight but, where the anhydrous sodium silicate content is at the extreme upper end of the range for that ingredient, and tetrasodium pyrophosphate is added in proportions in excess of 15% for improving the molding characteristics, it may be necessary to decrease the soda ash content to an amount even below 20%.

Where the presence of a surface active agent, such as the previously mentioned synthetic detergent and wetting agents, is desirable, a maximum of about 5% has been found sufficient for most purposes where a detergent in briquetted form can advantageously be adopted. Usually smaller proportions are sufficient. When a proportion as high as 5% is employed, most satisfactory physical structure is obtained where the anhydrous sodium silicate content does not exceed about 15% by weight and the molar ratio of metasilicate to orthosilicate present approximates unity or, in other words, the alkalinity approaches that of the sesquisilicate. Even when smaller proportions of such surface active agents are employed, briquettes of better physical structure are obtained when the sodium silicate con-

stituent consists of the sesquisilicates or a mixture of the meta and ortho silicate.

The following formulae are presented as specific illustrations of proportions of the several constituents which have been used with advantage in the preparation of my improved briquettes. It will be understood, however, that my invention is not limited to a product prepared from the particular formulae shown. In each instance the proportions are by weight. For convenient reference to the compositions of the resultant briquette, which subsequently appear, the respective formulae have been consecutively numbered.

	Batch No.						
	1	2	3	4	5	6	7
Trisodium phosphate (dodecahydrate).....	10	10	35	10	20	5	10
Water glass, 41° Bé.....	20	20	5	30	1.5	10	20
Caustic soda.....	8.8	8.8	1.4	13.2	.4	6.4	8.8
Tetrasodium pyrophosphate.....		10	15	10	10	10	10
Soda ash.....	45.7	37	29.6	28.7	43.7	44.6	33.5
Surface active agent.....				8.1	24.4	24.0	2.5
Added water.....	15.5	14.2	14				15.2

The composition of the briquettes resulting from the compounding and molding of the detergent mixture, in accordance with the process herein described, was as tabulated below, the several products being identified with the formulae from which each was prepared by the consecutive numbering. The proportions are expressed as percentage by weight and, with respect to solid matter, are reported on an anhydrous basis.

	Batch No.						
	1	2	3	4	5	6	7
Trisodium phosphate.....	4.7	4.7	16.4	4.7	9.4	2.4	4.7
Sodium silicate.....	14.6	14.6	2.9	22	0.9	8.8	14.6
Tetrasodium pyrophosphate.....		10	15	10	10	10	10
Soda ash.....	45.7	37	29.6	28.7	43.7	44.6	33.5
Surface active agent.....				35	36.0	34	2.5
Total water (approx.).....	35	34	36				35

In the product of the above specific Examples 1, 2, 4 and 7, the alkalinity of the sodium silicate constituent approximated that of the sesquisilicate. In the product of Examples 3 and 5, the alkalinity was that of the metasilicate and in Example 6 the alkalinity was that of the orthosilicate. In the specific Example 7 the particular surface active agent used was that previously referred to as being sold under the tradename "Orvus."

While my invention is not predicted upon any theory with respect to the reasons for the unique physical characteristics of my improved briquettes, my investigations indicate that their physical structure results, at least in part, from the formation of crystals of mixed salts of the trisodium phosphate, the carbonate and the silicate with inclusions of greater or less amounts of other constituents present in the mixture. The crystals of mixed salts appear to be definite crystalline substances, though I am not prepared to state with certainty their composition. They appear to have approximately the following composition:

	Percent
Trisodium phosphate.....	6
Sodium carbonate.....	4
Sodium silicate.....	40
Water.....	50

My investigations also indicated that these crystals contain inclusions of sodium carbonate monohydrate. Sodium silicate in various stages of hydration has also been found around the crystalline masses.

Under some conditions, these crystals grow to considerable size, while under other conditions their presence is hardly visible. The size of the crystal growth appears to be influenced mainly by the sodium silicate content of the melt. In general, the crystal size increases with an increase in the percentage of sodium silicate. At the upper limit of the range of this ingredient, the crystals develop to a size that is visibly evident and, when excessive amounts of sodium silicate are used, the crystals are so large and loosely interlaced that the resulting briquette has impaired mechanical strength. This effect is more evident where the alkalinity of the silicate approaches that of the orthosilicate.

My observations also appear to indicate that other conditions being the same, an increase in the trisodium phosphate content tends to reduce the size of these crystals. These two opposing influences on crystal growth suggest the possibility of relationship between crystal size and molding time and offer a possible explanation of the improved physical structure of my briquettes. I have observed that the molding time is noticeably increased when the sodium silicate content is near the upper limit of the range where the resulting crystal growth is noticeably excessive in size and, as previously stated, there is a general tendency toward decreased molding time when the trisodium phosphate content is increased which increase I believe tends to decrease the size of the crystals.

Though I have herein described and claimed a process which I have found particularly advantageous in the preparation of my improved briquettes, it will be understood that my invention, with respect to the improved product, is not restricted to a product made by the particular process herein described. Likewise, though I have described my improved briquettes as adapted for use with mechanical washers, it will be understood that they are generally useful where a detergent in briquette form is desirable.

This application is in part a continuation of my co-pending application Serial No. 389,619, filed April 21, 1941.

I claim:

1. A detergent briquette chemically and physically stable, hard, strong and non-deliquescent consisting of a dense crystalline aggregate consisting essentially of the following constituents in proportions by weight within the respective indicated ranges: trisodium phosphate about 1% to 15%, sodium silicate about 1% to 25%, sodium carbonate about 20% to 50%, tetrasodium pyrophosphate about 3% to 25% and water about 30% to 40%, the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of the silicate being not less than 1:1 nor greater than 2:1.
2. A detergent briquette chemically and physically stable, hard, strong and non-deliquescent consisting of a dense crystalline aggregate consisting essentially of the following constituents in proportions by weight within the respective indicated ranges: trisodium phosphate about 1% to 15%, sodium silicate about 1% to 25%, sodium carbonate about 20% to 50%, tetrasodium pyrophosphate about 3% to 15%, an alkali-stable non-saponaceous, synthetic, organic, surface active agent 0% to about 5%, and water about 30% to

40% the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of the silicate being not less than 1:1 nor greater than 2:1.

3. A detergent briquette chemically and physically stable, hard, strong and non-deliquescent consisting of a dense crystalline aggregate consisting essentially of the following constituents in proportions by weight within the respective indicated ranges: trisodium phosphate about 1% to 15%, sodium silicate about 1% to 25%, sodium carbonate about 20% to 50% tetrasodium pyrophosphate about 3% to 25%, an amount of an alkali-stable non-saponaceous, synthetic, organic, surface active agent effective substantially to reduce the dissolving rate of the briquette and not exceeding about 5% and water about 30% to 40% the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of the silicate being not less than 1:1 nor greater than 2:1.

4. A detergent briquette chemically and physically stable, hard, strong and non-deliquescent consisting of a dense crystalline aggregate consisting essentially of the following constituents in proportions by weight within the respective indicated ranges: trisodium phosphate about 1%

to 15%, sodium carbonate about 20% to 50%, tetrasodium pyrophosphate about 3% to 25%, water about 30% to 40% and sodium silicate about 1% to 25%, the alkalinity of the latter approximating that of sodium sesquisilicate.

5. A detergent briquette chemically and physically stable, hard, strong and non-deliquescent consisting of a dense crystalline aggregate of approximately the following composition by weight: trisodium phosphate 4.7%, sodium carbonate 37%, tetrasodium pyrophosphate 10%, water 34% and sodium silicate 14.6%, the alkalinity of the latter approximating that of sodium sesquisilicate.

6. A detergent briquette chemically and physically stable, hard, strong and non-deliquescent consisting of a dense crystalline aggregate of approximately the following composition by weight: trisodium phosphate 16.4%, sodium carbonate 29.6%, tetrasodium pyrophosphate 15%, water 36%, sodium silicate 2.9%, the alkalinity of the latter approximating that of sodium metasilicate.

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