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DETERGENT BRIQUETTE

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The invention relates to improved briquetted detergent compositions and more particularly to detergent briquettes characterized by a unique combination of detergent characteristics and other physical and chemical properties which make them highly satisfactory for use in mechanical washing operations.

Modern mechanical methods and apparatus for washing dishes, milk cans and the like, particularly where operation is continued 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 on 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 material 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; that the briquette 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 operations 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 material be such as to avoid harmfully affecting the material being washed either by attacking the material or 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 mixtures 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 temperature required to fuse the detergent or detergent mixtures has 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 the fusion point or at temperatures necessary for fusing other desirable constituents.

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This temperature requirement has not permitted the incorporation in detergent mixtures so produced of many effective water conditioners and surface active agents, such as synthetic organic detergents 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 the natural hardness of the water supply and the tendency to form scale on the inner surface of the mechanical washers with which the detergent is used. Rapidity of this scale formation depends upon the degree and nature of hardness of the water and, in general, increases with the concentration of the 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 lesser extent with the cleansing operation.

The presence of water conditioners, such as the water conditioning polyphosphates, for instance tetrasodium pyrophosphate ($Na_4P_2O_7$), sodium tetraphosphate ($Na_6P_4O_{13}$), sodium tripolyphosphate ($Na_5P_3O_{10}$) and sodium hexametaphosphate ($Na_6P_6O_{18}$) 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, such as the non-saponaceous, organic, synthetic detergents, has been found further to enhance the cleansing action and to effect improved rinsing. However, for the reasons stated above, the incorporation of these materials in such anhydrous detergent briquettes formed by fusion at high temperatures 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 portion thereof 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 such detergent blocks in detergent operations. However, so far as I am aware, the detergent blocks produced according to the prior literature of the art have fallen short of the requirements essential to their satisfactory commercial use in mechanical washing operations.

I have previously discovered that detergent briquettes having desirable physical characteristics may be produced at moderate temperatures which permit incorporation therein of water conditioners and surface active agents, such as previously mentioned, by the use of various ingredients including silicates in proportions within rather definite ranges. However, in certain mechanical washing operations, and for other specialized purposes, the use of a detergent containing a silicate may be objectionable.

As distinguished from detergent briquettes of that general type containing a silicate as an essential ingredient, the briquette of my present invention need contain no silicate whatever, though unobjectionable small proportions of silicate may be included where desirable.

I have now discovered that briquettes having the required physical properties and especially suitable for use in mechanical washing operations, may be prepared, free from silicates, from detergent mixtures comprising borax, water and either trisodium phosphate or soda ash or both, in proportions within the limits herein defined without resort to high fusion temperatures, and that, when so compounded, various surface active agents, such as the synthetic detergents and water conditioning polyphosphates, such as previously noted, may be incorporated in the briquette without destroying its desirable physical properties.

The detergent mixtures, of which the briquettes of my present invention are composed, consist essentially of either trisodium phosphate or soda ash, a borate, and water. Advantageously, it may also contain a water conditioning polyphosphate, such as previously noted, though the presence of such polyphosphate is not essential to the production of a briquette having the desired physical properties. While it is not essential that both trisodium phosphate and sodium carbonate be used, the presence of both is frequently advantageous in detergent operations, and where desired, both may be included in the briquettes of my present invention without detrimentally affecting their physical properties. The detergent mixtures of the present invention further include the presence of one or more synthetic organic detergents.

Where a detergent of higher alkalinity is desired, caustic soda may be added to the detergent mixture in amounts approximating those required to give an alkalinity equivalent to that of the metaborate. Where a lower alkalinity is required, a relatively small proportion of sodium bicarbonate may be added to the mixture. At higher alkalinity, the presence of some trisodium phosphate is desirable in order to attain optimum molding conditions.

Caustic soda and borax may thus be used in proportions equivalent to sodium metaborate, for instance, as well as other borates of intermediate composition obtained by the action of caustic on ordinary borax.

The proportion of the several ingredients may be varied over a considerable range, as herein specified, to meet specific detergent requirements. However, in order to obtain briquettes having the desired physical properties, it is necessary that the range of variation of proportions of the several ingredients be kept within rather well-defined limits.

In the preparation of my briquettes, the trisodium phosphate constituent may be introduced in the form of the ordinary commercial hydrated product, generally represented by the formula $Na_3PO_4.12H_2O$. Theoretically, this material contains 56.8% water. However, repeated analysis indicates 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 used for the different proportions of water contained therein. Also, materials which react under the compounding conditions to form trisodium phosphate, for instance disodium phosphate and caustic soda, may be substituted for an equivalent proportion of the trisodium phosphate, appropriate allowance being made for the water content of such reacting materials and water produced by the reactions.

As previously noted, trisodium phosphate need not be used in my present briquettes. On the other hand, it may be used in proportions ranging up to as high as about one-half the formula weight.

The sodium carbonate constituent of my briquette, when used, may conveniently be supplied as anhydrous soda ash and the proportion and ranges of proportions specified herein are based on the use of sodium carbonate in that form. However, it may be supplied in the form of a hydrate, such as a mono- or decahydrate, appropriate allowance being made for the differences in compositions. Similarly, the sodium carbonate may be supplied in the form of materials, such as sodium bicarbonate and caustic soda, which react under the compounding conditions to form sodium carbonate.

The proportion of the sodium carbonate constituent of my improved briquette is subject to considerable latitude of variation to meet particular detergent requirements. As previously noted, the sodium carbonate constituent may be entirely omitted, if desired. On the other hand, sodium carbonate may be incorporated in my briquette in proportions ranging as high as about one-half of the formula weight.

Where either trisodium phosphate or soda ash is omitted, the other should be used in an amount not less than about one-tenth the formula weight. Similarly, where both are used, the amount should aggregate not less than about one-tenth of the formula weight. The aggregate amount of these two materials may range as high as about one-half the formula weight.

Similarly, polyphosphates are not essential constituents of the briquettes of my present invention but one or more of the water-conditioning polyphosphates, such as previously noted, may usually be incorporated with advantage. Where polyphosphates are to be incorporated in my briquettes, I have found that proportions of about 15% by weight are usually sufficient for

most water-conditioning purposes and proportions of any one or more of said polyphosphates aggregating about 15% of the formula weight may be incorporated in these briquettes without destroying their desirable briquetting properties. However, where either tetrasodium pyrophosphate or sodium tripolyphosphate is used alone or in conjunction with the other polyphosphates noted, a total amount of the polyphosphates in excess of 15% may with advantage be incorporated in the briquettes, say up to about 50%, without seriously affecting detrimentally the molding time or the physical structure of the resulting briquette provided not more than about 15% of these other polyphosphates is used. This 15% proportion may be increased to about 20% provided there is a preponderance of tetrasodium pyrophosphate present.

The amount of water present in the detergent composition is of major importance with respect to molding time and mechanical structure of the resulting briquette. It is also of importance with respect to the active detergent content of the briquette. I have found the permissible range of proportions of water in my briquetted product to be from about 30% to 50%. Within this range of proportions, the water may be varied without encountering any destructive effect on the physical structure of the briquette. However, I have found that proportions of water approaching the lower limit of this range, say about 30% to 35%, result in more desirable pouring, congealing and structural characteristics of the resulting briquette. The less desirable conditions generally encountered as the proportion of water approaches the upper limit of this range may, to a considerable extent, be corrected by using proportions of trisodium phosphate in the upper portion of the prescribed range for that constituent.

In determining the quantity of water, if any, to be added as such in the compounding of my briquettes, due consideration must be given to the amount of water present in the various constituents either as water of crystallization or otherwise, and the water formed by chemical reaction. Also, a small amount of water may be vaporized or lost during compounding of detergent mixtures. However, if compounded by the process herein described, the amount of water thus lost is usually of no particular consequence. If the amount of water thus lost is excessive, additional water may be added to the batch.

The proportion of the borax constituent of my briquette calculated as anhydrous borax may be varied from as low as about 1% to as high as about 30%. As the proportion of the borax constituent approaches the lower limit of this range, I have generally observed an increase in the required molding time which is particularly noticeable where no trisodium phosphate is present. This tendency may to a considerable extent be corrected by the use of higher proportions of the trisodium phosphate constituent. Where no trisodium phosphate is used, it is generally preferable to use an amount of borax in the upper half of the prescribed range in order to obtain the optimum molding characteristics. Also, where the proportion of borax is in the lower part of the range, improved molding characteristics are obtained by the addition of one or more of the sodium polyphosphates herein noted. Also, where no trisodium phosphate is used, the desirable proportion of borax for molding characteristics may be decreased by the inclusion of a sodium polyphosphate, particularly tetrasodium pyrophosphate or sodium tripolyphosphate.

An important aspect of my present invention is my ability to control, to a very substantial extent, the solubility rate of my briquettes. This aspect of the invention is particularly advantageous where the briquetted product is to be used in mechanical washers, for example, with hot water. Where such use is anticipated, the solubility rate of the briquette may be decreased by increasing the proportions of the borate constituent and, conversely, where an increased solubility rate is desirable, this may be effected by reducing the proportion of the borate constituent.

I have further found that the solubility rate of the briquette may be materially reduced by incorporating in the briquette a rather small proportion of the borate constituent supplemented by a small proportion of a sodium silicate of relatively low alkalinity. Thus, by the combined use of the borate and the silicate, the solubility rate of the briquette may be reduced to a greater extent than is effected by the use of a comparable amount of either of these materials alone.

The borate constituent is preferably added in the form commercially known as borax and which has the formula $Na_2B_4O_7.10H_2O$.

The compounding of my improved detergent briquette is advantageously effected generally in accordance with the process described in my copending application Serial No. 582,575, filed March 13, 1945.

As therein described, the compounding operation is advantageously carried out in a conventional steam-jacketed kettle equipped with a stirring device. Excellent results in preparing and duplicating the composition and structure of the briquettes have been obtained by adhering to the following general procedure: The trisodium phosphate, borax, caustic soda, or sodium bicarbonate, or such of these as are to be used, and additional water, if any, in predetermined amounts, are first added to the kettle. The mixture is heated and agitated until the mass is fluid and has assumed its maximum clarity, at which time the soda ash or the polyphosphate, or both, are added, if such is to be used. The mixture is then drawn off or poured into molds. During the mixing and pouring the mixture is maintained at a temperature below that at which substantial evolution of steam would occur with the resultant material loss in water. Higher temperatures are to be avoided as it is desirable to reduce to a minimum the amount of water lost during the compounding operation and to avoid decomposition of less stable ingredients. By minimizing the water lost during the compounding operation, the proportion of water in the product may be effectively controlled by regulation of the total amount of water added to the bath. The maximum temperature to which the material is heated depends primarily upon the concentration of the solution in the fluid mass but it is usually found to be within the range of about 70° C. to about 100° C.

As pointed out hereinbefore, a particularly advantageous characteristic of the briquettes of my invention is the presence of a non-saponaceous, organic, synthetic detergent. These synthetic detergents comprise the alkali-stable anionic, cationic and non-ionic organic surface active agents. The anionic synthetic detergents include the acids and salts of organic compounds

containing long chains of carbon atoms such as the sulfated alcohols, the aryl polysulfonates and the alkylated aryl sulfonates. Suitable examples of anionic agents comprise sodium dioctyl sulfosuccinate, sodium sulfoethyl stearamide, sodium tetrahydronaphthalene sulfonate, sodium butyl diphenyl sulfonate, potassium tri-isopropyl naphthalene tri-sulfonate, the sodium salt of sulfated lauryl alcohol, and sodium "keryl" benzene sulfonate wherein the "keryl" radical (as described and defined in U. S. patent to Flett, No. 2,364,782) is a combination of saturated aliphatic hydrocarbon radicals principally of straight chain structure and derived from chlorinated kerosene. The sodium "keryl" benzene sulfonates may be defined more specifically as sodium alkyl benzene sulfonates the alkyl side chain of which is derived from a kerosene fraction having an average content of between 7 and 19 carbon atoms per molecule. The cationic synthetic detergents include particularly the quaternary ammonium and pyridinium salts such, for example, as lauryl dimethyl benzyl ammonium chloride, octadecyl dimethyl benzyl ammonium chloride, cetyl trimethyl ammonium bromide, lauryl pyridinium chloride, and benzyl trialkyl ammonium chloride wherein the alkyl radical is that derived from commercial lauryl alcohol. The non-ionic synthetic detergents include the condensation products of alkylolamines with fatty acids generally having from 10 to 16 carbon atoms, and the polyether alcohols. Diethyl aminoethyl oleylamide acetate, the condensation product of commercial lauric acid (C_{10} to C_{16}, and predominately C_{12} fatty acids) with ethanolamine (the product comprising hydroxy ethyl lauramide,

$$C_{11}H_{23}CONHCH_2CH_2OH$$

in the case of the C_{12} acid), and hydroxy ethyl polyethoxy ethyl ether,

$$C_2H_5O(CH_2CH_2O)_nCH_2CH_2OH$$

where n is an integer of the order of 8 to 12, are examples of suitable non-ionic synthetic detergents.

In preparing the briquettes containing one or more of such organic synthetic detergents, the detergent is preferably added to the briquette composition just prior to pouring. The synthetic detergents are effective when added to the briquette composition in amounts ranging from about 0.25% to about 5% of the anhydrous active ingredient by weight of the briquette composition. Within this range, amounts of synthetic organic detergents ranging from about 1% to about 2% give particularly satisfactory results.

I have observed that where the amount of borax or of the surface active agent approaches the upper limit of the prescribed range, there is a tendency toward a relatively more fluid mass in the kettle, and that under such conditions the proportion of water may be reduced slightly below 30% and still permit satisfactory pouring.

After all of the desired ingredients have been added and thoroughly mixed, as previously noted, the mixture is drawn off into suitable molds and allowed to cool until the briquette has developed sufficient mechanical strength to permit its removal from the mold. For the briquettes of my present invention the maximum molding time generally varies from about one hour to several hours depending upon the composition of the mixture. On cooling, detergent

compositions of this type seem to expand somewhat and this, combined with their tendency to adhere to metal surfaces, has previously presented difficulty in the molding of detergent materials. By using flexible briquette molds, such as molds made of rubber or similar material, as described in the above-referred-to co-pending application, these difficulties are eliminated.

My invention will be further described and specifically illustrated by the following examples of proportions and ranges 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 the invention is not limited to products prepared from the particular formula shown. In each instance, the percentages given are the percentages by weight of the briquette composition and are on the anhydrous basis.

Example	1	2	3	4	5	6
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Na_3PO_4	20.0	25.0	58.0	26.2	------	20.0
Na_2CO_3	13.0	32.0	------	16.2	44.0	13.0
$Na_4B_4O_7$	31.5	1.0	5.0	10.6	10.0	31.0
H_2O	35.0	40.0	35.0	35.0	35.0	35.0
Synthetic A	------	------	1.0	1.0	1.0	------
Synthetic B	0.5	1.0	1.0	1.0	------	------
Synthetic C	------	0.5	------	------	------	------
Synthetic D	------	0.5	------	------	------	------
Synthetic E	------	------	------	------	------	1.0
$Na_4P_2O_7$	------	------	------	------	10.0	------
$Na_6P_6O_{18}$	------	------	------	10.0	------	------

In the briquette compositions referred to in the foregoing table, "synthetic A" comprised a hydroxy ethyl polyethoxy aryl ether appearing to aproximate the formula

$$C_4H_9C_6H_4O(CH_2CH_2O)_{10}CH_2CH_2OH$$

"Synthetic B" comprised benzyl alkyl dimethyl ammonium chloride wherein the alkyl group consisted of a commercial lauryl alcohol residue, "synthetic C" comprised sodium "keryl" benzene sulfonate wherein, as described hereinbefore, the "keryl" group was derived from chlorinated kerosene and comprised the aliphatic saturated predominately straight chain hydrocarbons of kerosene, "synthetic D" was another hydroxy ethyl polyethoxy aryl ether appearing to approximate the formula

$$C_8H_{17}C_6H_4O(CH_2CH_2O)_8CH_2CH_2OH$$

and "synthetic E" comprised the condensation product of commercial lauric acid (C_{10} to C_{16}, and predominately C_{12}) with ethanolamine.

In each of the foregoing examples, the briquetted product was physically stable, hard, strong and non-deliquescent, and satisfactory for use in mechanical washing operations.

Though I have described my improved briquettes as particularly adapted for use with mechanical washers, it will be understood that they are generally useful where detergents in briquetted form are desirable.

This application is a continuation in part of my application Serial No. 606,484, filed July 21, 1945.

I claim:

1. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-

tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of a non-saponaceous alkali-stable organic synthetic detergent.

2. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 1–2% of a non-saponaceous alkali-stable organic synthetic detergent.

3. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of a non-saponaceous alkali-stable organic synthetic anionic detergent.

4. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of a sodium alkyl benzene sulfonate the alkyl side chain of which is derived from a kerosene fraction having an average content of between 7 and 19 carbon atoms per molecule.

5. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of a non-saponaceous alkali-stable organic synthetic cationic detergent.

6. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of lauryl dimethyl benzyl ammonium chloride.

7. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of a non-saponaceous alkali-stable organic synthetic non-ionic detergent.

8. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 50% of a sodium polyphosphate including not more than about 15% of the polyphosphate of the group consisting of sodium tetraphosphate and sodium hexametaphosphate, and about 0.25–5% of hydroxy ethyl lauramide.

9. A detergent briquette 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: total water about 30–50%, at least one detergent of the group consisting of sodium carbonate and trisodium phosphate aggregating from about one-tenth to about one-half the total formula weight, about 1–30% of a sodium borate, up to about 15% of a sodium polyphosphate, and about 0.25–5% of a non-saponaceous alkali-stable organic synthetic detergent.

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