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DETERGENT BRIQUETTE

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4 Claims. (Cl. 252—137)

The present invention relates to the preparation of a water-soluble detergent briquette, which readily disintegrates when agitated in water, but yet possesses sufficient strength and cohesiveness to withstand the jars and shocks attendant handling, packaging and transporting without fracturing, crumbling, or rubbing off of surface material. More particularly, the composition of the briquette contains a detergent mixture, including a unique organic nonsoap surfactant and a condensed phosphate, useful in heavy-duty mechanical washing operations, such as the washing of cotton textiles.

The use of detergent in briquette form, such as tablets, balls, or wafers, in mechanical washing operations, such as laundry washing machines, is desirable for several reasons. For example, the bulk density of the detergent is much greater in this form than for the corresponding powder, thus permitting much space-saving in the matter of shipping and storing. The powder form is plagued with the problem of offensive dust which has undesirable physiological effects when breathed even in trace amounts. As compared with detergents in the liquid form, detergents in briquette form create no dripping problem. Further, detergent in briquette form is not wasted through spillage, and is adapted to being dispensed in the right amount without measuring.

Known washing agents, such as the readily available alkyl benzene sulfonates, soap, and the like, in tablet form for use in mechanical washing operations suffer from certain serious disadvantages, the most significant of which has to do with the rate of solution. For example, although alkylbenzene sulfonate detergent by itself dissolves readily, it no longer has a solubility rate such as to permit its use in these operations when briquetted. On the other hand, briquetted surfactant of the type herein contemplated unexpectedly possesses a good rate of solution in water. Similarly, soap is not only deficient in solubility characteristics, but in addition, has inferior wetting and detersive action. As can be seen, therefore, good washing machine tablets or briquettes are required to be strong, i.e., will not break or crumble easily due to physical shock, and to be quick-dissolving in water, i.e., readily disintegrable in the agitation provided by conventional washing machines. In addition, a good briquette must be pleasant to the touch; for example, it is not sticky. The briquettes prepared in accordance with the present invention possess the desirable characteristics of a satisfactory briquette.

The detergent briquette herein contemplated consists essentially, by weight, based on the briquette, of 15 to 80, preferably 20 to 30, percent water-soluble normal primary alkyl alkali metal or alkaline earth metal or ammonium sulfonate detergent component, the alkyl groups containing 10 to 20 carbon atoms and averaging 12 to 18 carbon atoms; 25 to 75 percent, preferably 40 to 60, water-soluble condensed inorganic phosphate detergent salt builders, and 5 to 20 percent, preferably 7 to 12, water. Further, the

sum of the weights of the aforesaid components constitute at least 70 percent of the briquette weight.

Desirably, the briquette contains other components or ingredients normally associated with heavy-duty synthetic formulations. Thus, up to about 30 percent of the briquette weight can be constituted of special purpose additives or inert extenders, such as antiredeposition agents, anticorrosion agents, sequestering agents, foam stabilizers or boosters, optical bleaches, inert inorganic salts, such as the sulfates, borates, carbonates and the like.

The alkyl sulfonate detergent component specified above is one in which the alkyl group is essentially a straight chain, has a carbon content averaging 12 to 18 carbon atoms, and is of primary nature, i.e., has the sulfonic acid group attached to terminal carbon atom. These sulfonates can be prepared in accordance with known methods involving the free radical addition of a bisulfite ion-yielding salt, for example, sodium or potassium bisulfite, ammonium bisulfite, calcium bisulfite, and magnesium bisulfite. Preferably employed are the alkali metal sulfonates. Also satisfactory are mixtures of these with an alkaline earth metal sulfonate, such as the calcium sulfonate, in amounts ranging, for example, from 25 to 75 parts alkali metal sulfonate, and the balance calcium sulfonate based on one hundred parts, by weight, of combined sulfonates.

Conveniently, the 1-olefin employed in the bisulfite addition reaction is obtained by the cracking of petroleum wax or petroleum distillates whereby a fraction of 1-olefins of essentially straight-chain structure having 10 to 20 carbon atoms can be obtained, the various molecular species being present in approximately equal molecular proportions. Further, if desired, various smaller olefin fractions for the production of the sulfonate can be obtained within the C_{10}–C_{20} range, as by distillation to produce fractions of desired carbon content or molecular weight, whereby to obtain a sulfonate having an average carbon content in the range about 12 to 18, as hereinabove mentioned.

In accordance with one way of producing the alkyl sulfonate detergent component, bisulfite is added to the appropriate olefin material in an aqueous methanol or ethanol solvent at a temperature of 65° C. to 75° C. and in the presence of an initiator, for example, a peroxide. Following the sulfitation reaction, a deoiling step is performed to remove unreacted hydrocarbons. These can be removed by extraction with a light hydrocarbon, for example, pentane, or by dilution with water to effect phase formation of the oil and a water-alcohol solution of the sulfonate, followed by separation of the phases, as by decantation.

At this stage, the alkyl or paraffin sulfonate contains appreciable amounts of inorganic sulfate, e.g., sodium sulfate, in an amount up to about 25 percent by weight. As indicated, however, the presence of this inorganic sulfate does not adversely affect the final briquette. But if desired, the inorganic sulfate, e.g., sodium sulfate, formed during reaction, can be removed by desalting. This can be accomplished by adjusting the alcohol content of the solution to about 65 to 75 volume percent based on total volume of alcohol and water, and in such proportions as to maintain a sulfonate concentration in the range 5 to 15 weight percent of the total. Upon standing, sodium sulfate crystals precipitate and are removed by filtration. When proceeding as thus described, the content of inorganic sul-

fate in the sulfonate active can be reduced to below 5 percent.

The alcohol is then removed from the sulfonate solution by distillation. Heating is continued to remove more water until the water content of the product is about 20 to 25 weight percent of the mixture. At this point, the product, a thick slurry which is still flowable at about 100° C., is dropped upon a chilled roll, whereupon the product solidifies. The material is then chipped off the roll, and air-dried in a conventional dryer to an extent calculated to give the amount of moisture desired in the finished briquette, as determined, for example, by the Karl Fischer titration method.

The condensed phosphate component of the briquette can be defined as those polyphosphates commonly used in conjunction with synthetic surfactants to produce heavy-duty detergent compositions, and are often referred to as builders for the synthetic surfactant. They can be used in their commercially available anhydrous form, obtained by the high-temperature dehydration of the orthophosphates tripolyphosphates, from a mixture of disodium orthophosphate and monosodium orthophosphate; tetrasodium pyrophosphates, from disodium orthophosphate; and sodium polymetaphosphates, from orthophosphate. The various condensed phosphates can be used singly or in admixture. As is known in the detergent art, the proportions of the various phosphates are frequently altered in practice. The proportions can vary in the present case also. Generally, good results are obtained when tripolyphosphate is essentially the sole condensed phosphate, or is admixed with the other condensed phosphates, for example, 80 percent tripolyphosphate and 20 percent pyrophosphate.

Thus, far, two of the essential components of the briquettes, namely, the paraffin sulfonate organic synthetic detergent and condensed phosphate builder, have been described. The third essential component is water, the presence of which is important in imparting the necessary plasticity to the mixture constituting the briquette. The water thus serves to facilitate compounding and to render the mixture moldable, whereby a cohesive, physically strong form-retaining mass of the desired shape, can be produced. Accordingly, the amount of water is such as to impart plasticity to the ingredients, and to permit compacting or molding. In general, the proportions of water will range from 5 to 20, preferably 7 to 12, percent of the briquette weight. In determining the water content, any water associated with the separate components due to water or hydration, or to the manufacturing process, or otherwise, is included.

During the compounding operation, other ingredients, compatible with the essential components of the briquette, in combined amounts up to about 30 weight percent of the briquette, can be incorporated. Examples of compatible opional ingredients are certain detergent active materials, such as the alkylaryl sulfonates, alcohol sulfates, polyoxyethylene alkylphenol sulfates, acylisethionates, sulfonated fatty acid monoglycerides, polyethylene glycols, C_{12}–C_{16} fatty alcohols, stearic acid, mineral oil, and polyethylene glycol (4,000) monostearate.

Other compatible optional ingredients which are particularly useful in the preparation of the briquettes herein contemplated are those customarily present in heavy-duty detergent formulation. These include, in weight amounts, based on the briquette: an anticorrosion and stabilizing agent, such as sodium silicate, wherein the SiO_2 to Na_2O ratio can range from 1/2 to 2/1, in proportions of, for example, 5 percent; an antiredeposition agent, such as sodium carboxymethyl cellulose, as described for example, in U.S. Patent No. 2,568,334, proportions of about 1 to 3 percent being cited as illustrative; a foam modifier, such as a mono- or di-ethanolamide of a fatty acid, such as lauric isopropanolamide, in proportions, for example, of 5 percent; a chemical bleaching agent, such as sodium perborate or sodium percarbonate, for example, in an amount of 2 to 5 percent; optical whiteners, in amounts of the order of 0.1 to 0.2 percent, such as the triazinyl and aroylstilbenes, benzidinesulphones, bisbenzimidazoles, triazoles, and amino coumarins; sequestering agents, in amounts, for example, or the order less than one percent, such as tetrasodium ethylene diamine tetraacetic acid; finally, certain inorganic salts, up to about 30 percent, such as inorganic sulfate, carbonate, or borate.

The compounding of the aforesaid components can be effected by mixing the dry ingredients with water. Enough water is added to give a final mixture containing water within the specified range, for example, 10 percent. If desired, in order to ensure intimate admixture, a milling step, as is known in the art, may be used. Or, if desired, the various ingredients can be wet-mixed until a homogeneous, stirrable, flowable mixture is obtained (approximately 50 percent water). This mixture can then be dried, for example, by heating, until the desired water content is present.

It has been found that the mechanical procedure for making the tablets is not critical. For example, satisfactory briquettes have been prepared by hand-fashioning and placing the composition in a mold having the desired shape, and then using a hammer to impart the necessary cohesive strength. Another satisfactory method is to place the desired amount of briquette-forming composition in a press, after which applying pressure to impart cohesiveness to the mass.

In so operating, it has been found that pressures of the order of 250 p.s.i. to 700 p.s.i. are sufficient to render the shaped mass cohesive, and to produce a briquette having a satisfactory solution rate. When so proceeding, sturdy briquettes capable of withstanding handling shocks can be produced, as shown, for example, by impact-strength determinations. Thus, when operating in the specified pressure range, briquettes were obtained having impact resistances of the order of 0.09 to 0.17 foot-pound (Izod test using a Baldwin machine, specimens one-inch wide by one-half inch thick).

As indicated, satisfactory briquettes are required to have good solution characteristics. This may be determined by measuring the weight of the briquette periodically as it dissolves in agitated water, or alternatively by measuring the quantity of detergent active material dissolved in the water. In the examples that follow, these determinations were carried out in a Dexter washing machine containing 56 liters of water at 120° F. and having a hardness of 50 p.p.m. (calcium and magnesium salts in the ratio of 2 parts calcium chloride to 1 part magnesium chloride, calculated as the carbonate, in the indicated amount in de-ionized water).

Determinations were made every minute or two. The rate of solution was calculated by plotting the percent weight dissolved as a function of time, extrapolating the curve to 100 percent solution, and then noting the corresponding point on the time scale. The percent rate of solution is then found by dividing 100 percent by this total time to solution.

A satisfactory briquette is one which completely dissolves before the expiration of the washing cycle, typically less than about 10 minutes, in a conventional washing machine.

The paraffin sulfonates of the following examples, unless otherwise indicated, were prepared from a mixture of cracked wax olefins containing 10 to 20 carbon atoms in a straight chain. The molecular species were present in approximately equal proportions, and the average carbon content of the material was approximately 15.

Example 1

63 parts of sodium paraffin sulfonate and 27 parts of tetrasodium pyrophosphate were mixed and then milled several times with 10 parts of water. The milled material was then compaced and stamped in a mold to give a circular tablet 1½ inches in diameter, ⅜-inch thick,

and weighing about 17 grams. The wafer was tested in a Dexter washing machine, as hereinabove described, and the following data obtained:

Time (minutes):	Weight percent dissolved
0	0
2	38
4	65
6	85
10	100

The extrapolated plot of the above data indicated complete solution at seven minutes; therefore, the average rate of solution is 100/7 or 14.2 percent per minute.

A wafer was prepared substantially in accordance with the procedure outlined above, except that the sodium paraffin sulfonate was replaced by an equal amount of a commercially available sodium polypropylenebenzene sulfonate, the polypropylene groups having an average of 12 carbon atoms in the chain. The final wafer weighed about 17 grams. In this case, only 90 percent solution was obtained after 20 minutes; therefore, the rate of solution is 90/20 or 4.5 percent per minute.

Another wafer was similarly prepared except that the sodium paraffin sulfonate was replaced by an equal amount of a commercial soap. Solution was only 75 percent complete after 20 minutes; therefore, the rate of solution is 75/20 or 3.8 percent per minute.

It will be noted from the above comparisons that the wafer prepared in accordance with the present invention dissolves much more readily than one prepared from commercial soap or a commercial detergent.

Example 2

Three wafers were prepared as in Example 1, except that the tetrasodium pyrophosphate was replaced by an equal amount of sodium tripolyphosphate. The following results were obtained:

Time (Minutes)	Active Component in Wafer, Weight Percent Dissolved		Ivory Soap
	Sodium Paraffin Sulfonate	Sodium Polypropylene-benzene Sulfonate	
2	35	12	15
4	60	25	28
6	85	33	35
10	100	60	60
20	----------	85	85

The average rate of solution of the sodium paraffin sulfonate detergent was calculated to be about 15 percent per minute, whereas the other wafers had a rate of solution less than seven percent per minute.

That the rapid solution of the paraffin sulfonate detergent tablets is independent of builder concentration is shown in Examples 3 and 4, in which large amounts of builder are compounded with a small amount of sodium paraffin sulfonate.

Example 3

A wafer was prepared according to the procedure outlined in Example 1, from 18 parts sodium paraffin sulfonate, 72 parts of tetrasodium pyrophosphate, and 10 parts of water. The final wafer weighed about 17 grams. This wafer was tested in the washing machine test and found to dissolve at the following rate:

Time (minutes):	Weight percent dissolved
0	0
2	30
4	55
6	75
10	100

The extrapolated time for 100 percent solution is 8½ minutes, or an average rate of 12 percent per minute.

The same experiment was repeated except that the sodium paraffin sulfonate was replaced by sodium polypropylenebenzene sulfonate. This tablet had an average rate of solution of seven percent.

A third like experiment with Ivory soap in the place of sodium paraffin sulfonate showed only 50 percent solution after 20 minutes of agitation, i.e., less than three percent per minute.

Example 4

Three similar tablets were made as in Example 3, except that the tetrasodium pyrophosphate was replaced by sodium tripolyphosphate. The following results were obtained:

Time (Minutes)	Active Component in Wafer, Weight Percent Dissolved		Ivory Soap
	Sodium Paraffin Sulfonate	Sodium Polypropylene-benzene Sulfonate	
2	28	15	12
4	55	30	22
6	75	42	28
10	95	50	42
20	100	70	65

The rate of solution of sodium paraffin sulfonate was about nine percent per minute for tablets of this composition; this is about twice as fast for the tablets containing soap or alkylbenzene sulfonate as the active detergent material.

Other common detergent additives may also be included in the tablet, and yet those made from paraffin sulfonates will dissolve faster than those made from other detergents or soap, as shown in Examples 5 and 6.

Example 5

A composition was prepared by mixing sodium paraffin sulfonate, 27 parts; tetrasodium pyrophosphate, 45 parts; silicate G, 4.5 parts; carboxy methyl cellulose, 0.9 part; sodium sulfate, 12.6 parts; and water, 100 parts. The mixture was heated on a steam plate to drive off the water until the water content was 10 percent. Following the procedure of Example 1, two sample bars weighing 19 grams and 60 grams, respectively, were prepared. The weights of the bars after testing in the Dexter machine, as outlined above, are as follows:

Time (Minutes)	Weight (Grams)		Weight Percent Dissolved	
	Large	Small	Large	Small
0	60	19	0	0
1	45	15	25	21
2	26	10	56	48
3	Bars broke and the test was discontinued			

The rate of solution based on the initial two minutes was 28 percent and 24 percent per minute for the large and small bars, respectively.

Tablets made from ammonium paraffin sulfonates and other heavy-duty builders also show this rapid solution as compared with other detergents or soap.

Example 6

A large bar was prepared according to Example 5, with essentially the same quantities of the same ingredients as in Example 5, except that the sodium paraffin sulfonate was replaced by ammonium paraffin sulfonate.

In this case, the washing machine test gave the following results:

Time (Minutes)	(Grams)	Weight Percent Dissolved
0	62.5	0
1	47	24
2	34	45
3	21	67
4	8	85
5	0	100

The rate of solution in this case was about 22 percent per minute, very similar to the rate for sodium paraffin sulfonate of Example 5. A bar of the same composition as above, except that the ammonium paraffin sulfonate was replaced by sodium polypropylbenzene sulfonate, had a solution rate of only six per cent per minute.

The following examples illustrate that a bar using a C_{15}–C_{20} sodium paraffin sulfonate has about the same rate of solution as one prepared from a C_{10}–C_{20} sodium paraffin sulfonate.

Example 7

Compositions were prepared by dry-mixing 20 parts of the appropriate sodium paraffin sulfonate, 50 parts of tetrasodium pyrophosphate, 5 parts silicate G., 1 part carboxy methyl cellulose, 24 parts of sodium sulfate; the water content being then adjusted to 10 percent by weight of the total.

Tablets weighing approximately 42 grams, were prepared in a hand press, average pressure 500 p.s.i. These tablets were tested in a Dexter washing machine, as previously described, and showed the following characteristics:

Time (Minutes)	Paraffin Sulfonate in Wafer (Weight Percent Dissolved)	
	C_{10}–C_{20}	C_{15}–C_{20}
0	0	0
1	38	38
2	72	67
5	92	92
10	100	100

The rate of solution is about 18 percent per minute for either tablet.

That the rate of solution is relatively independent of the pressure used in making the detergent tablet is shown in Example 8.

Example 8

Tablets were made by the procedure of Example 7, except that each tablet was molded at a different pressure,

using C_{10}–C_{20} sodium paraffin sulfonate as the active ingredient. Solubility in the Dexter test was as follows:

Time (Minutes)	Pressure of Molding (p.s.i.) (Weight Percent Dissolved)			
	280	420	570	710
0	0	0	0	0
1	47	40	32	36
2	89	78	61	70
5	100	100	94	91
6			100	100

The calculated average rates of solution for tablets molded at 280, 420, 570, and 710 p.s.i. were 20, 20, 17, and 17 percent per minute, respectively. Thus, an increase in the pressure of the molding operation by a factor of 2 or 3 changes the time of complete solution by only one minute and the rate of solution by only 3 percent per minute.

We claim:

1. A water-soluble briquette comprising an intimate admixture compacted in the presence of 5 to 20 percent of water at a pressure in the range 250 to 700 pounds per square inch to form the finished briquette, said briquette consisting essentially of, by weight, 15 to 80 percent water-soluble normal primary alkyl sulfonate detergent salt selected from the group consisting of the alkali metal, alkaline earth metal and ammonium salts, the alkyl group containing 10 to 20 carbon atoms and averaging 12 to 18 carbon atoms, 25 to 75 percent water-soluble inorganic condensed sodium phosphate detergent builder, and the 5 to 20 percent of water which was present during the compacting step.

2. A detergent briquette according to claim 1, wherein the alkyl sulfonate detergent is the sodium salt.

3. A detergent briquette according to claim 1, wherein the alkyl sulfonate detergent is present in an amount of 20 to 30 percent; the water-soluble inorganic sodium phosphate detergent builder, in an amount of 40 to 60 per cent; and the water, 7 to 12 percent.

4. A detergent briquette according to claim 3, wherein the alkyl sulfonate detergent is the sodium salt.

References Cited in the file of this patent

UNITED STATES PATENTS

2,356,903	Wood	Aug. 29, 1944
2,374,187	Flett	Apr. 24, 1945
2,504,411	Harman	Apr. 18, 1950
2,781,321	Mayhew et al.	Feb. 12, 1957
2,875,155	Miles	Feb. 24, 1959
2,956,026	Lew	Oct. 11, 1960
3,001,948	Clippinger	Sept. 26, 1961

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,172,859 March 9, 1965

Douglas F. Percival et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 34, for "Thus," read -- Thus --; line 49, for "or", first occurrence, read -- of --; line 55, for "opional" read -- optional --; column 4, line 5, for "or" read -- of --; line 74, for "compaced" read -- compacted --; column 6, line 4, after "by" insert -- a --.

Signed and sealed this 27th day of July 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents