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WASHING COMPOSITIONS AND PROCESS

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ABSTRACT OF THE DISCLOSURE

Water soluble sulfites and bisulfites are used to increase washing effectiveness of detergent compositions, especially those containing bacterial protease and/or bacterial amylase, and to give a buffered pH level, particularly where other components give too high a pH which would normally affect the stability of said enzymes.

BACKGROUND OF THE INVENTION

In recent years the detergent industry has been making strenuous efforts to provide new and improved detergents and especially detergents having improved washing efficiency. Many articles have been published on this subject as, for example, "The World of Synthetic Detergents," CW Report, Part One, published in Chemical Week for Sept. 20, 1969, pp. 69-74, 78, 80, 89, 91, 93, 94, and 96; "The World of Synthetic Detergents" CW Report, Part Two, Chemical Week for Oct. 29, 1969, pp. 80-86, 91, 92, 94, 95, 97, and 98; "Detergent Ingredients' Effect on Enzymes," published in Soap and Chemical Specialties for September 1969, pages 60, 62, 64, 66, 70, 82, 84, and 90; "NTA Gets Big Push in Detergent Powders," published in Chemical and Engineering News, Apr. 6, 1970, page 11; and "Nonionics In the '70's," published in Detergents and Specialties, May 1970, pages 33-36.

It may be noted that the use of enzymes, especially bacterial protease and/or bacterial amylase, in washing compositions has increased dramatically in the last five years, due to the fact that washing efficiency can be increased by the use of such enzymes. Tests for washing efficiency have been developed based on the use of an instrument known as a Terg-O-Tometer. In general these tests involve washing a pretreated swatch of cloth in various types of washing solutions and determining the average reflectance (percent white) before and after washing. The difference, which is usually referred to as ΔR_d is a measure of the effectiveness of a given laundry product. The greater the ΔR_d , the greater the effectiveness of such product. A laboratory scale multiple washing machine which simulates the action of the agitator-type home washer is used for the test. The conditions set forth in this procedure for laboratory operations are precise and practical and there is a high degree of reproducibility of the test data. Two types of swatches are used which are usually called BMI and CMS. The BMI swatches are impregnated with blood, milk and India ink and are used where it is desired to determine the effectiveness of bacterial protease enzymes. The CMS swatches are impregnated with cocoa, milk and starch and are used where it is desired to determine the effectiveness of bacterial amylase enzymes.

Detergents are normally composed of surface active agents and chelating agents with or without foam boosters, anti-soil redeposition agents, silicates, optical brighteners, borates, enzymes, fillers, organic solvents, coloring agents and perfume. Sodium tripolyphosphate (herein called STP) is the principal chelating agent employed in most present day detergents but recently phosphates have come under attack because of their effect on plant life in streams and ponds and efforts have been made to replace at least a part of the phosphates with other substances, for example, trisodium nitrilotriacetatemonohydrate

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(herein called NTA). This has resulted in compositions that dissolve in water to give a higher pH. The increased alkalinity tends to destroy the stability of the enzymes used in washing compositions and render them less effective. It would therefore be desirable to provide washing compositions and a washing process containing ingredients which make it possible to improve washing efficiency over a relatively wide alkaline pH, especially compositions containing bacterial protease and/or bacterial amylase and to give a buffered pH level, particularly where other components give too high a pH which would normally affect the stability of such enzymes.

OBJECTS

In view of the foregoing desiderata, one of the objects of the present invention is to provide new and improved washing compositions and a washing process by adding to a detergent composition or to the wash water, especially to detergent compositions or wash waters containing bacterial protease and/or bacterial amylase, an ingredient which gives a buffered pH level, particularly where other components give too high a pH which would normally affect the stability of such enzymes, and which when employed in the proper proportions enhances the washing efficiency.

A more specific object of the invention is to provide new and improved washing compositions and a new and improved washing process in which water soluble sulfites and bisulfites are employed to increase the washing effectiveness of detergent compositions, especially those containing bacterial protease and/or bacterial amylase. Other objects will appear hereinafter.

BRIEF SUMMARY OF THE INVENTION

In accordance with the invention water soluble sulfites and/or bisulfites, preferably sodium sulfite (Na_2SO_3), sodium bisulfite (NaHSO_3), and/or sodium meta bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), are added to detergent compositions containing surface active agents and chelating agents with or without other ingredients, or to wash waters containing such compositions, in sufficient amount to increase the washing efficiency and preferably also in amounts sufficient to give a buffered pH level particularly where other components give too high a pH which would normally affect the stability of bacterial protease and/or bacterial amylase enzymes where such enzymes are present in such compositions or in wash waters involving the use of such compositions.

The invention particularly contemplates detergent compositions and wash water wherein the pH is around 8 to 12.0 and especially when it is within the range of 9.0 to 10.5.

DETAILED DESCRIPTION OF THE INVENTION

Most of the detergents today contain surfactants, STP and fillers as the principal ingredients. STP is a sequestering agent for calcium and magnesium salts normally found in hard water. It is a member of the class of materials usually known as chelating agents. NTA is another member of this class of materials which also includes the disodium salt of ethylene diamine tetraacetic acid, the tetrasodium salt of ethylenediamine tetraacetic acid, the sodium salts of N-(hydroxyethyl)ethylenediamine tetraacetic acid, and the sodium salts of diethylenetriaminepentaacetic acid. Substances such as STP and NTA are sometimes referred to in the art as "builders." The surfactants are sometimes referred to as "actives."

Among the surfactants commonly employed are C_{13} alkyl benzene sulfonate, and 85/15 tallow/coconut soap, a C_{12-15} primary alcohol with 9 moles of ethylene oxide, a polyoxypropylene-ethylene oxide condensate with an approximate molecular weight of 1750 and containing

about 80% ethylene oxide, and a cationic surfactant, dimethyldicoccammonium chloride.

The most commonly used filler is sodium sulfate. Other fillers are sodium carbonate, sodium sesquicarbonate, sodium bicarbonate and sodium borate.

Other adjuvants are foam boosters (e.g., lauryl alcohol and cocomonoeethanolamide); antisoil redeposition agents (e.g., sodium carboxymethyl cellulose); anticorrosion agents (e.g., sodium silicate); optical brighteners; bleaches (e.g., sodium perborate); and enzymes. The following table, Table I, gives a more specific breakdown of the composition of detergents contemplated in the practice of the present invention, it being understood that a water soluble sulfite and/or bisulfite is added to such detergents or to wash waters containing them in amounts sufficient to enhance the washing efficiency. While sodium sulfite, sodium bisulfite and/or sodium metabisulfite are preferred, the corresponding water soluble potassium salts can be used but are normally too expensive for practical purposes. Other sulfites which are water soluble and substantially equivalent to sodium sulfite, sodium bisulfite and/or sodium bisulfite can also be employed.

TABLE I

Composition of detergent	Percent by weight	
	General	Preferred
Surfactants.....	3-40	3-20
Foam booster.....	0-12	0-12
Chelating agents.....	2-75	30-75
Antisoil redeposition agent.....	0-1	0-1
Silicates.....	0-20	0.02-10
Optical brighteners.....	0-1	0-1
Borates.....	0-5	0-2
Perborates.....	0-30	0-30
Enzymes.....	0-5.0	0.1-1.2
Fillers.....	0-70	10-25
Organic solvents.....	0-9	0-9
Coloring agents.....	0-0.2	0-0.2
Perfume.....	0-0.3	0-0.2

The water soluble sulfite, bisulfite and/or metabisulfite preferably constitutes 0.2 to 0.6 part of the detergent. The amount used should be sufficient to produce at least 300 parts per million (p.p.m.) of water soluble sulfite, bisulfite and/or sodium meta-bisulfite in a wash water and preferably at least 400 p.p.m., calculated as Na_2SO_3 . Usually enhanced effectiveness is not obtained beyond 1000 p.p.m. and in most cases no improvement in effectiveness is obtained when the amount is greater than 800 p.p.m. It should be noted that sodium meta-bisulfite reacts in equal molar proportions with water to form 2 moles of sodium bisulfite. The invention contemplates the use of mixtures of sodium sulfite and sodium bisulfite (or sodium metabisulfite) so as to give the wash water a buffered pH usually not exceeding 10 and in most cases not exceeding 9.8. The optimum washing pH range is usually from about 8 to 10. The usual recommended concentration of detergent in the wash water is 1500 p.p.m. (0.15% weight/volume).

The following table gives compositions in terms of the major components of various enzyme based detergent products, some of which are used in the specific examples hereinafter given. It will be understood that these compositions also contain as minor components carboxymethyl cellulose, optical brighteners, bleach stabilizers, perfumes, dyes and free moisture. In the table the quantities are given in parts by weight.

TABLE II

	A	B	C	D	E	F	G	H	I
STP.....	64	72	49	50		30	40	27	33
Sodium perborate 4H ₂ O.....		19			16	22		18	25
Surfactants.....	8.0	7	17	16.5		17	9.5	18	16.5
Sulfate solution.....	12.0		17	11		14		13	11.0
Borax.....	2.0		1						
Sodium bicarbonate.....						28			
Filler (sodium sulfate).....	13.4		15.5	21.7		16.3	21.9	23.4	13.9
Enzyme.....	0.6	2	0.5	0.8	0.6	0.7	0.6	0.6	0.6

The following table illustrates the potency of various commercially available enzymes.

TABLE III

Example	Enzyme activity per gram	
	Protease, PV/gram	Amylase, DV/gram
M.....	113,600	
N.....	100,000	15,000
O.....	30,000	27,500
P.....	122,400	<200
Q.....	126,200	<200
R.....	117,300	30,500

It will be understood that the potency of the enzymes can vary rather widely. Thus enzymes containing bacterial protease and/or bacterial amylase can be prepared in powdered form having activities within the range of 15,000 to 1,000,000 PV units per gram and 30 to 100,000 DV units per gram. Normally the enzyme powders contain diluents so that the enzyme activity per gram as added to a detergent base is within the range of 15,000 to 150,000 PV units per gram and 0 to 150,000 DV units per gram.

The following table illustrates specific formulations for a high STP detergent, an NTA-low STP detergent and a low STP detergent using a combination of two of the enzymes given in Table III.

In the table the quantities are given in parts by weight.

TABLE IV

	J	K	L
STP.....	70.00	34.50	34.50
NTA.....	0.00	24.80	0.00
Coloring agent.....	0.13	0.13	0.13
Non-ionic and brightener.....	5.00	4.00	4.00
Perfume.....	0.20	0.20	0.20
Enzyme O.....	0.50	0.50	0.50
Enzyme M.....	0.25	0.25	0.65
Na ₂ SO ₃	23.92	35.62	60.02
Total.....	100.00	100.00	100.00

The invention is further illustrated but is not limited by the following examples in which the quantities are given by weight unless otherwise indicated. In these examples washing efficiencies were determined with various types of detergents with and without sodium sulfite in various proportions. BMI or CMS test swatches were used (6" x 3"). Three swatches were used for each BMI test and five swatches were used for each CMI test. The washing cycle was 10 minutes at 120° F. The rinse cycle was 5 minutes at 100° F. and pH values are those of the wash solutions at the end of the wash cycle. The reflectance was determined with a Hunter D25 Color Reflectometer and the ΔR_d readings represent the difference in reflectance before and after each test. The readings were based on average readings taken three times on one side and three times on the other side of each swatch. The concentration of detergent in every case was 0.15% (w/v.) which corresponds to 1500 p.p.m., unless otherwise indicated. All of the wash tests described in the following examples were carried out with city water from Milwaukee, Wis., having a hardness of 135 p.p.m.

EXAMPLE 1

In this example the detergent used was a commercial detergent base known as "White Magic." The tests were carried out with and without a fixed percentage of sodium carbonate and with and without various percentages of sodium sulfite. No enzyme was added to the detergent. The following results were obtained.

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Percent (w./v.) ingredient in wash			Percent (w./w.) enzyme added to detergent		BMI test cloths	
Sodium carbonate	Sodium sulfite				pH	ΔR_d
None	None	None	None		9.1	24.1
0.02	None	None	do		9.7	23.0
0.02	0.04	None	do		9.7	25.6
0.02	0.08	None	do		9.7	26.0

It will be noted that an increase in the alkalinity reduced the efficiency from 24.1 to 23.0 but the addition of sodium sulfite in the amount of 0.04% more than compensated for this by raising the efficiency to 25.6. The addition of 0.08% sodium sulfite further enhanced the effectiveness of the detergent.

EXAMPLE 2

The procedure was the same as in Example 1 except that the detergent base was the NTA-low phosphate detergent base K of Table IV without the enzyme. The following results were obtained.

Ingredients added per liter of wash solution					
Percent (w./v.) ingredient in wash			Percent (w./w.) enzyme added to detergent		
Sodium carbonate	Sodium sulfite				
None	None	None	None		9.25
0.02	None	None	do		9.75
0.02	0.04	None	do		9.75
0.02	0.08	None	do		9.7

Here again it will be noted that the loss of efficiency due to increase in alkalinity was more than compensated for by the addition of the sodium sulfite.

EXAMPLE 3

The wash tests were carried out with combinations of enzymes and STP and NTA with and without the addition of sodium carbonate and sodium sulfite. The following results were obtained.

Ingredients added per liter of wash solution						
STP (g.)	NTA (g.)	Sodium carbonate (g.)	Sodium sulfite (g.)	Enzyme		CMS test cloths
				M, mg.	O, mg.	
1.0	None	None	None	3.75	7.50	8.6
1.0	None	None	0.4	3.75	7.50	8.6
1.0	None	0.2	None	3.75	7.50	9.5
1.0	None	0.2	0.4	3.75	7.50	9.6
0.5	0.5	None	None	3.75	7.50	9.25
0.5	0.5	None	0.4	3.75	7.50	9.25
0.5	0.5	0.2	None	3.75	7.50	9.75
0.5	0.5	0.2	0.4	3.75	7.50	9.7

EXAMPLE 4

The procedure in this example was similar to the procedure in Example 3 except that BMI test cloths were used instead of CMS test cloths and only enzyme M (Table III) was added. The results obtained were as follows:

Ingredients added per liter of wash solution					
STP (g.)	NTA (g.)	Sodium carbonate (g.)	Sodium sulfite (g.)	Enzyme M (Table III)	MI test cloths
1.0	None	None	None	7.5	8.7
1.0	None	None	0.4	7.5	8.6
1.0	None	0.2	None	7.5	9.5
1.0	None	0.2	0.4	7.5	9.6
0.5	0.5	None	None	7.5	9.3
0.5	0.5	None	0.4	7.5	9.25
0.5	0.5	0.2	None	7.5	9.8
0.5	0.5	0.2	0.4	7.5	9.8

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Comparing the test results of Example 3 with those of Example 4 it will be observed that there was an enhanced efficiency when the sodium sulfite was added where the wash water contained one gram per liter of STP at pH's of 8.6 or 8.7 and also at pH's of 9.5 and 9.6. At a pH of 9.25 when a combination of 0.5 g. of STP and 0.5 g. of NTA was used per liter of wash water there was no significant improvement with the CMS test cloths but there was a very substantial improvement with the BMI test cloths. Also, there was a significant improvement with both types of test cloths at higher pH values of 9.7 and 9.8.

EXAMPLE 5

In the following series of sixteen tests, the first four tests were carried out with White Magic detergent base, the next four tests with Punch detergent base, the next four tests with Tide detergent base and the last four tests with Colgate-Palmolive NTA-low phosphate detergent base. Enzyme M (Table III) was added in all of these tests.

Percent (w./v.) ingredient in wash			Percent (w./w.) enzyme M added to detergent		BMI test cloth	
Sodium carbonate	Sodium sulfite				pH	ΔR_d
None	None	0.5	None		9.05	37.0
0.02	None	0.5	None		9.65	34.9
0.02	0.04	0.5	None		9.65	36.9
0.02	0.08	0.5	None		9.6	37.6
None	None	0.5	None		8.75	35.4
0.02	None	0.5	None		9.7	33.5
0.02	0.04	0.5	None		9.6	35.0
0.02	0.08	0.5	None		9.6	35.4
None	None	0.5	None		8.95	40.7
0.02	None	0.5	None		9.70	37.8
0.02	0.04	0.5	None		9.70	38.3
0.02	0.08	0.5	None		9.65	39.1
None	None	0.5	None		9.3	35.6
0.02	None	0.5	None		9.75	32.4
0.02	0.04	0.5	None		9.75	34.0
0.02	0.08	0.5	None		9.80	34.1

All of the tests show that the washing efficiency decreases at higher pH's with detergents containing enzymes but the addition of sodium sulfite in quantities of 0.04% and 0.08% improves the washing efficiency at such pH's.

EXAMPLE 6

In this example the washing tests were carried out with Axion pre-soak base which was added to the wash water in an amount of 0.1% (w./v.). The following results were obtained.

Percent (w./v.) ingredient in wash			Percent (w./w.) enzyme M added to detergent		BMI test cloth	
Sodium carbonate	Sodium sulfite				pH	ΔR_d
None	None	0.5	None		8.55	34.0
0.02	None	0.5	None		9.6	31.6
0.02	0.04	0.5	None		9.6	33.6
0.02	0.08	0.5	None		9.6	33.4

Again, it will be seen that the increase in pH reduced the washing efficiency but that the addition of sodium sulfite improved the washing efficiency at the higher pH.

EXAMPLE 7

The series of tests illustrated in this example were carried out with White Magic detergent base with the addition of various enzymes. The results were as follows.

Percent (w./v.) ingredient in wash		Percent (w./w.) enzyme added to detergent	BMI test cloths	
Sodium carbonate	Sodium sulfite		pH	ΔR_d
None	None	0.5 M	9.05	37.0
0.02	None	0.5 M	9.65	34.9
0.02	0.04	0.5 M	9.65	36.9
0.02	0.08	0.5 M	9.6	37.6
None	None	0.5 P	9.1	35.1
0.02	None	0.5 P	9.7	37.0
0.02	0.04	0.5 P	9.7	35.2
0.02	0.08	0.5 P	9.65	35.3
None	None	0.5 Q	9.1	37.3
0.02	None	0.5 Q	9.7	34.5
0.02	0.04	0.5 Q	9.7	37.2
0.02	0.08	0.5 Q	9.7	36.9
None	None	0.5 R	9.1	36.7
0.02	None	0.5 R	9.65	36.2
0.02	0.04	0.5 R	9.65	37.6
0.02	0.08	0.5 R	9.65	38.4

It will be seen that these test results are generally similar to those described in the previous examples and show that enhanced washing efficiency is obtained by the addition of sodium sulfite, regardless of the source of the enzymes.

EXAMPLE 8

This example illustrates the results obtained by combining a particular type of enzyme with White Magic detergent base with and without sodium carbonate and/or sodium sulfite. The results were as follows.

Percent (w./v.) ingredient in wash		Percent (w./w.) enzyme R added to detergent	BMI test cloths	
Sodium carbonate	Sodium sulfite		pH	ΔR_d
None	None	0.5	9.1	36.7
0.02	None	0.5	9.65	36.2
0.02	0.04	0.5	9.65	37.6
0.02	0.08	0.5	9.65	38.4
CMS test cloths				
None	None	0.5	8.95	28.4
0.02	None	0.5	9.55	26.0
0.02	0.04	0.5	9.55	27.9
0.02	0.08	0.5	9.5	28.1

In each case the addition of the sodium sulfite at the higher pH gave an enhanced washing efficiency.

EXAMPLE 9

In this series of tests a combination of enzymes was employed with a Colgate-Palmolive NTA-low phosphate detergent with the addition of various proportions of sodium sulfite. The results obtained were as follows.

Percent (w./w.) sodium sulfite in wash	Percent (w./w.) enzyme added to detergent		CMS test cloths	
	Enzyme M	Enzyme O	pH	ΔR_d
None	0.25	0.50	9.4	26.3
0.01	0.25	0.50	9.4	26.3
0.02	0.25	0.50	9.4	26.3
0.04	0.25	0.50	9.4	28.8
BMI test cloths				
None	0.50	None	9.55	35.3
0.02	0.50	None	9.70	35.2
0.04	0.50	None	9.70	36.4
0.08	0.50	None	9.65	36.4

These results show that no improved washing efficiency was obtained at 0.02% sodium sulfite but a very significant improvement was obtained at 0.04% sodium sulfite.

EXAMPLE 10

In this series of tests two different enzymes were combined with a detergent base containing the ingredients listed for detergent base L in Table IV excluding the enzymes. The results were as follows.

Percent (w./v.) sodium sulfite in wash	Percent (w./w.) enzyme added to detergent		CMS		BMI	
	Enzyme M	Enzyme O	pH	Rd	pH	ΔR_d
None	0.25	0.50	9.3	21.3	9.35	29.3
0.04	0.25	0.50	9.3	22.7	9.35	31.4
0.08	0.25	0.50	9.25	24.3	9.35	30.6
None	0.65	0.50	9.3	24.9	9.25	32.7
0.04	0.65	0.50	9.25	26.4	9.3	34.2
0.08	0.65	0.50	9.35	26.1	9.35	34.1

It will be seen that the addition of 0.04% sodium sulfite gave a significant improvement.

EXAMPLE 11

In this series of tests a specific enzyme M (Table III) was added to an NTA-low phosphate detergent base having a composition corresponding to that of detergent K in Table IV, exclusive of the enzymes. The results were as follows.

Percent (w./v.) ingredient in wash		Percent (w./w.) enzyme M added to detergent	BMI test cloth	
Sodium carbonate	Sodium sulfite		pH	ΔR_d
None	None	0.5	9.1	32.2
0.01	None	0.5	9.5	31.2
0.01	0.04	0.5	9.5	32.6
0.01	0.08	0.5	9.5	33.0
None	None	0.5	9.1	34.0
0.02	None	0.5	9.75	32.4
0.02	0.04	0.5	9.75	33.1
0.02	0.08	0.5	9.75	33.4

Again it will be noted that at the higher pH the addition of the sodium sulfite increased the washing efficiency.

EXAMPLE 12

In this series of tests the procedure was the same as that in Example 11 except that a combination of enzymes was employed. The results were as follows.

Percent (w./v.) ingredient in wash		Percent (w./w.) enzyme added to detergent		BMI test cloths	
Sodium carbonate	Sodium sulfite	Enzyme M	Enzyme O	pH	ΔR_d
None	None	0.25	0.50	9.15	31.0
0.01	None	0.25	0.50	9.55	28.8
0.01	0.04	0.25	0.50	9.5	31.1
0.01	0.08	0.25	0.50	9.5	31.0
None	None	0.25	0.50	9.2	30.2
0.02	None	0.25	0.50	9.8	27.3
0.02	0.04	0.25	0.50	9.8	29.5
0.02	0.08	0.25	0.50	9.75	29.5
None	None	0.25	0.50	9.2	29.6
0.04	None	0.25	0.50	10.05	25.9
0.04	0.04	0.25	0.50	10.05	28.1
0.04	0.08	0.25	0.50	10.0	27.6

From the foregoing results it is evident that the addition of the sodium sulfite enhanced the washing efficiency at pH's from 9.5 to 10.05.

EXAMPLE 13

In this series of tests the procedure was the same as in Examples 11 and 12 except that CMS cloths were used. The results were as follows.

Percent (w./v.) ingredient in wash		Percent (w.w.) enzyme added to detergent		CMS test cloth	
Sodium carbonate	Sodium sulfite	Enzyme M	Enzyme O	pH	ΔR_d
None.....	None	0.25	0.50	9.0	28.1
0.01.....	None	0.25	0.50	9.5	27.2
0.02.....	None	0.25	0.50	9.7	24.8
0.04.....	None	0.25	0.50	9.95	22.9
None.....	None	0.25	0.50	9.0	28.0
0.01.....	None	0.25	0.50	9.4	27.2
0.01.....	0.04	0.25	0.50	9.4	28.5
0.01.....	0.08	0.25	0.50	9.4	28.8
None.....	None	0.25	0.50	9.0	29.3
0.02.....	None	0.25	0.50	9.7	26.6
0.02.....	0.04	0.25	0.50	9.7	29.4
0.02.....	0.08	0.25	0.50	9.65	28.9
None.....	None	0.25	0.50	9.0	29.4
0.04.....	None	0.25	0.50	10.0	24.4
0.04.....	0.04	0.25	0.50	10.0	25.7
0.04.....	0.08	0.25	0.50	9.95	26.0

These results clearly show that the addition of sodium sulfite enhanced the washing efficiency.

EXAMPLE 14

In this series of tests enzyme M (Table III) was added to White Magic detergent base and various proportions of sodium carbonate, sodium sulfite and sodium bisulfite were employed. The results were as follows.

Percent (w./v.) ingredient in wash			Percent (w./w.) enzyme M added to detergent	BMI test cloth	
Sodium carbonate	Sodium sulfite	Sodium bisulfite		pH	ΔR_d
None.....	None	None	0.5	9.05	38.2
0.02.....	None	None	0.5	9.7	36.0
0.02.....	0.04	None	0.5	9.8	37.8
0.02.....	0.03	0.01	0.5	9.4	37.3
None.....	None	None	0.5	9.0	38.1
Do.....	0.03	0.01	0.5	8.55	40.7
Do.....	0.02	0.02	0.5	8.15	40.0
Do.....	0.01	0.03	0.5	7.8	36.2
0.02.....	None	None	0.5	9.75	37.0
0.02.....	0.03	0.01	0.5	9.4	39.5
0.02.....	0.02	0.02	0.5	9.05	40.1
0.02.....	0.01	0.03	0.5	8.7	40.5

These test results show that the combination of sodium sulfite and sodium bisulfite is effective in enhancing washing efficiency, except in one instance where the pH was 7.8.

EXAMPLE 15

The following tests were carried out with various commercial detergent bases and a pre-soak base without the addition of any enzyme and at pH's from 8.95 to 9.3 with and without the addition of sodium sulfite. The results were as follows:

Percent (w./v.) product in wash	Percent (w./v.) sodium sulfite in wash	Percent (w./w.) enzyme added to product	BMI test cloths	
			pH	R_d
0.15 White Magic... Detergent base...	None 0.04	None..... do.....	9.1 9.1	24.4 26.3
0.15 Punch..... Detergent base...	None 0.04	do..... do.....	9.0 9.0	19.3 21.5
0.1 Axion..... Pre-soak base.....	None 0.04	do..... do.....	8.95 8.95	17.9 21.0

These results show that the addition of the sodium sulfite gave a very significant improvement in washing efficiency.

From the foregoing examples it can be concluded that the use of a sufficient amount of sodium sulfite or its equivalent will enhance the washing efficiency of detergents and pre-soak bases of the type described significantly at various pH levels. Further, it can be concluded that while raising the pH, for example, by adding sodium carbonate, will reduce the washing efficiency, with or with-

out enzymes, this loss can be largely compensated for by adding sodium sulfite or its equivalents. Thus, by using sodium sulfite or its equivalent it is possible to employ detergents which are more alkaline. This also makes it possible to maintain a desirable washing efficiency by replacing at least a portion of the phosphates with other substances such as NTA, thereby avoiding the polluting effect of phosphates in disposal waters.

The sodium sulfite and/or sodium bisulfite or their equivalents can be added to the detergent base or to enzymes which are added to the detergent base or directly to the wash water. Usually, it is more practical to make a solid or liquid product in which all of the detergent ingredients are combined so that the user can add the proper proportions to the wash water.

The invention is hereby claimed as follows:

1. In a process of washing textile materials in water, the improvement which comprises adding to the wash water a quantity of a substance from the group consisting of water soluble sulfites, bisulfites, metabisulfites, and mixtures thereof sufficient to enhance the washing efficiency of said wash water while maintaining a pH within the range of 8 to 12 in said wash water.

2. A process as claimed in claim 1 in which the quantity of said substance is within the range of 300 to 1000 parts by weight, calculated as Na_2SO_3 , per million parts by weight of said wash water.

3. A process as claimed in claim 1 in which said substance is sodium sulfite and the quantity thereof is 400 to 800 parts per million parts of said wash water.

4. A process as claimed in claim 1 in which said wash water has a pH within the range of 9.0 to 10.5.

5. A process as claimed in claim 1 in which said wash water comprises sodium tripolyphosphate.

6. A process as claimed in claim 1 in which said wash water comprises trisodium nitrilotriacetate monohydrate.

7. A process as claimed in claim 1 in which said wash water comprises an enzyme from the group consisting of bacterial protease, bacterial amylase and mixtures thereof.

8. In a process of washing textile materials in water, the improvement which comprises adding to the wash water a quantity of a substance from the group consisting of sodium sulfite, mixtures of sodium sulfite with sodium bisulfite and mixtures of sodium sulfite with sodium metabisulfite, said quantity being within the range of 300 parts per million to 1000 parts per million and being sufficient to enhance the washing efficiency of said wash water while maintaining a pH within the range of 8 to 12 in said wash water.

9. A process as claimed in claim 8 in which said wash water contains a substance from the group consisting of surfactants, chelating agents, sodium sulfate, sodium carbonate, sodium sesquicarbonate, sodium bicarbonate, sodium borate, borax, sodium carboxy methyl cellulose, sodium silicate, sodium perborate, and enzymes from the group consisting of bacterial protease, bacterial amylase and mixtures thereof.

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195—63; 252—105, 158

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252-105

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,741,901 Dated June 26, 1973

Inventor(s) Jack Ziffer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Table I, under "Preferred", opposite "Coloring Agents", "0.0-2" should read -- 0.0.2 --.

Column 5, line 64, "MI" should read -- BMI --; line 72, in the table, under "STP(g.)", "0.0" should read -- 1.0 --.
1.5 0.5

Column 7, line 55, "CMSrtest" should read -- CMS test --.

Column 9, line 39, "40.5" should read -- 40.6 --

Column 10, line 67, "Scharz" should read -- Schwarz --.

Signed and sealed this 30th day of October 1973.

(SEAL) ✓
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents