United States Patent Office 3,549,539 Patented Dec. 22, 1970

3,549,539

DISHWASHING POWDERS

Leslie Albert Stanley Mallows, Wirral, England, assignor to Lever Brothers Company, New York, N.Y., a corporation of Maine

No Drawing. Filed Oct. 23, 1967, Ser. No. 677,079
Int. Cl. C11d 3/075, 7/56
U.S. Cl. 252—99 4 Claims

ABSTRACT OF THE DISCLOSURE

An improved nonionic surfactant based detergent powder for use in a machine dishwashing powder is obtained when the nonionic surfactant is a mixture of: (A) nonylphenol-5-EO or a condensation product of a random C_{11} to C_{15} secondary alcohol and ethylene oxide with an HLB value between 11.5 and 13.5; and (B) a polyethyleneoxide-polypropyleneoxide condensate that consists of between 5 and 25% polyethyleneoxide and 95 and 75% polypropyleneoxide and has a molecular weight between 1500 and 2700.

This invention relates to detergent powders. In particular it relates to a machine dishwashing powder.

In a dishwashing machine food soil is removed partly by mechanical action and partly by physico-chemical influences. The mechanical action normally takes place when the soiled surfaces of the load are deluged with wash liquor. Amongst the physico-chemical factors that affect the cleaning of dishes and cutlery are wetting, emulsification, work of adhesion of soiled substrate, alkalinity, oxidation potential, soil suspension, anti-flocculation and foam control.

The food soil may be present in a variety of states; some foodstuffs are oxidised, polymerised or partially decomposed by cooking, and this will affect the ease with which they may be removed.

The main foodstuffs are proteins, phospholipids, triglycerides and carbohydrates. Each of these probably responds in different ways to physical and chemical conditions. The foodstuff may coat widely different substrates, for example, glass, glazes (plain and pigmented) that coat pottery and chinaware, metals and plastics.

It will be appreciated from this that to formulate a successful dishwashing powder is very difficult. It is made more difficult by the fact that, in general, each of the functional properties of a formulation is due to a separate ingredient but that in a mixture the properties of each ingredient may be influenced by the others. Whereas an ingredient may be present to give a certain effect it may also have unwanted side effects such as counteracting the beneficial effects of other ingredients.

One particular problem in the formulation of a dishwashing powder if it is to be used in a dishwashing machine is foam. Foam interferes with the washing process in a dishwashing machine. For instance, it absorbs the energy of the wash liquor and so reduces the mechanical cleaning action and it also can cause dangerous overfoaming. A particular difficulty in selecting a suitable surfactant for use in a machine dishwashing powder is that the surfactant should control or depress foam formed by foodstuffs such as proteins.

In general, conventional anionic surfactants foam too much to be used in machine dishwashing powder formulations. Cationic surfactants absorb onto glass and ceramic surfaces to form hydrophobic films which lead to spotting, particularly in hard water, as the films dry. The use of nonionic surfactants in a machine dishwashing powder is therefore normally recommended.

It has been found that a machine dishwashing powder should contain between 0.5 and 10%, preferably 1 and 5%, by weight of a nonionic surfactant that in the Dynamic Ross-Miles Test, under conditions described hereafter, gives a foam height of less than 40 cms.

It has now been discovered that an improved detergent powder, particularly for use in a machine dishwasher, is obtained if the nonionic surfactant consists of a mixture of:

(A) Nonylphenol-5-EO or a condensation product of a random C_{11} to C_{15} secondary alcohol and ethylene oxide with an HLB value between 11.5 and 13.5; and

(B) A polyethyleneoxide-polypropylene oxide condensate that consists of between 5 and 25% polyethylene oxide and 95 and 75% polypropylene oxide and has a molecular weight between 1500 and 2700.

Both component A and component B must be dispersible or soluble in water at the concentrations used for a machine dishwashing powder, normally within the range 0.3 to 0.6% by weight.

By a random secondary alcohol is meant a mixture of straight-chain alcohols in which the hydroxy group is attached to differing carbon atoms. For example, a random C_{14} secondary alcohol contains C_{14} straight-chain alcohols in which the hydroxy group is attached to the C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13} and C_{14} carbon atoms.

Nonylphenol-5-EO is the condensate of nonylphenol with ethylene oxide which contains, on average, 5 moles of ethylene oxide.

A preferred composition according to the invention contains component A and component B in a ratio between 1:2 and 1:5.

A preferred condensation product for random, C_{11} to C_{15} secondary alcohol and ethylene oxide has an HLB value of 12.5.

A preferred polyethyleneoxide-polypropyleneoxide condensate consists of between 5 and 15% polyethylene oxide and 95 and 85% polypropylene oxide and has a molecular weight between 1900 and 2300.

The HLB value of an ethylene oxide condensate=$E/5$ where E is the weight percent of ethylene oxide in the condensate.

As well as surfactant a machine dishwashing powder will normally contain, by weight, 5 to 30% of a silicate, such as sodium metasilicate, 5 to 30% of an oxidising agent, 25 to 70% of a calcium-ion sequestrant and 1 to 20% of an inorganic filler salt, such as sodium carbonate or sodium sulphate.

Amongst the sequestrants that can usefully be used are sodium tripolyphosphate, trisodium nitrilotriacetate and tetrasodium ethylenediamine-tetraacetate. A preferred composition according to the invention contains between 40% and 65% sodium tripolyphosphate. When a more effective sequestrant is used a smaller proportion of sequestrant can be employed, for example trisodium nitrilotriacetate when used at a pH of 10 or above.

Typical oxidising agents are, for example, chlorinated sodium orthophosphate, chlorinated isocyanurates, and perborate with or without a copper catalyst or an activator such as sodium p-acetoxybenzene sulphate.

When a chlorine-containing oxidising agent is included in the formulation care must be taken to ensure that the other components of the formulation do not react disadvantageously with the oxidising agent.

From 0.1 to 1% by weight of an anti-tranishing agent such as stannous chloride, benzotriazole, sodium perborate benzimidazole and ferric chloride can usefully be included in the compositions according to the invention.

In the following examples the percentages are by weight and are expressed as anhydrous ingredient unless otherwise stated.

EXAMPLE I

The ability of various nonylphenol ethylene oxide condensates to emulsify fat was assessed as follows.

0.2 g. of nonylphenol *x*EO, where *x* is the mean number of moles of ethylene oxide per mole of nonylphenol, was mixed into 2 g. of fat. The mixture was poured into 100 ml. of hard water at 60° C. with stirring.

x:	Emulsification
4	Poor.
5	Very good.
6	Do.

EXAMPLE II

Machine dishwashing powders were prepared according to the following formulations:

Components	A, weight percent	B, C, D, weight percent
Sodium tripolyphosphate	45	45
Sodium metasilicate	18	18
Chlorinated sodium orthophosphate (hydrated)	18	18
Sodium carbonate	5	5
Polyethyleneoxide-polypropylene oxide condensate*	3.0	2.0
Nonylphenol *x*EO	0	1.0
Water	11	11

*10% polyethylene oxide and 90% polypropylene oxide; mol. wt. about 1,900 to 2,300.

In powders B, C and D *x* equals 4, 5 and 6 respectively.

Solutions of the powders A, B, C and D were prepared at 6 g. per litre in hard water (245 p.p.m. as $CaCO_3$).

Glass slides were dipped into the solutions and then withdrawn. Cooking fat had been previously agitated in the solutions which were maintained at 60° C.

It has been found that the appearance of the glass slides from the solutions of powders A, B and D was worse, larger droplets of oil etc., especially in the case of A than that of the glass slide from the solution of powder C.

EXAMPLE III

Powders B, C and D of Example II were tested for foaming. The following results were obtained:

Powder	Foaming	Percent rotor-speed ratio*
B	Slight overfoaming	67
C	No overfoaming	76
D	Overfoaming	67

*Ratio of rotor speed when rotor is immersed in a test solution with powder and standard soil present to the speed when rotor is immersed in water only, expressed as a percentage.

EXAMPLE IV

Machine dishwashing powders were prepared according to the following formulations:

	Components, weight percent						
	E	F	G	H	I	J	K
Sodium tripolyphosphate	45	45	45	45	45	45	45
Sodium metasilicate	15	15	15	15	15	15	15
Chlorinated sodium orthophosphate (hydrated)	20	20	20	20	20	20	20
Sodium carbonate	2	2	2	2	2	2	2
Nonylphenol-5-EO	3	2.5	2.0	1.5	1.0	0.5	0
Polyethyleneoxide-polypropylene oxide condendate*	0	0.5	1.0	1.5	2.0	2.5	3.0
Water	15	15	15	15	15	15	15

*10% polyethylene oxide and 90% polypropylene oxide; mol. wt. about 1,900 to 2,300.

The following results were obtained when the powders were tested for foaming:

Powder	Foaming	Percent rotor-speed ratio
E	Some overfoaming	37
F	do	52
G	do	59
H	do	59
I	No overfoaming	76
J	do	71
K	do	69

EXAMPLE V

Machine dishwashing powders were prepared according to the following formulations.

	Components, weight percent			
	L	M	N	O
Sodium tripolyphosphate	45	45	45	45
Sodium metasilicate	15	15	15	15
Chlorinated sodium orthophosphate (hydrated)	20	20	20	20
Sodium carbonate	2	2	2	2
Condensate of a random C_{11}—C_{13} secondary alcohol with ethylene oxide that contains, on average, 5 ethylene oxide moieties	1			
Condensate of a random C_{11}—C_{15} secondary alcohol with ethylene oxide that contains, on average, 7 ethylene oxide moieties		1		
Condensate of a random C_{11}—C_{15} secondary alcohol with ethylene oxide that contains, on average, 9 ethylene oxide moieties			1	
Condensate of a random C_{11}—C_{15} secondary alcohol with ethylene oxide that contains, on average, 13 ethylene oxide moieties				1
Polyethyleneoxide-polypropyleneoxidecondensate*	2	2	2	2
Water	15	15	15	15

* 10% polyethyleneoxide and 90% polypropyleneoxide; mol. wt. about 1,900 to 2,300.

The following results were obtained when the powders were tested for foaming:

Powder	Foaming	Percent rotor-speed ratio
L	Some overfoaming	65
M	No overfoaming	65
N	do	57
O	Gross overfoaming	

Dynamic Ross-Miles Test

6.4 g. of the nonionic synthetic detergent to be tested is dissolved or dispersed in 100 cc. of cold water. In order to aid dispersion the water is preferably ice-cold.

To 400 cc. of water heated to 50° C. are added the following ingredients:

	G.
Sodium tripolyphosphate	9.3
Sodium metasilicate pentahydrate	5.2
Sodium phosphate hypochlorite (chlorinated trisodium orthophosphate)	4.7

The addition must be slow and vigorous stirring must take place to prevent the tripolyphosphate forming a partial hydrate which would be difficult to dissolve. The solution obtained is cooled rapidly.

One egg at room temperature is placed in boiling water for 1 minute. The white is discarded together with fibrous attachments to the yolk. 14 g. of the yolk is dispersed in 70 cc. of water.

53 g. of potato powder is mixed into 250 cc. of hot water to give a smooth mix. 42 g. of cooking fat is then blended in.

10 cc. of the solution or dispersion of the nonionic synthetic detergent, the 400 cc. of the solution of tripolyphosphate etc., the 70 cc. of the dispersion of the egg yolk and 5.8 g. of the blend of potato powder and cooking fat in 250 cc. of water are added to 3520 cc. of cold water in a beaker. The 10 cc. of the solution of the nonionic synthetic detergent is equivalent to 3% of nonionic synthetic

detergent on a product basis under normal use. The water used in making solutions and the water in the beaker is artificially prepared hard water (245 parts per million as $CaCO_3$).

Into the solution so obtained in the beaker is inserted a vertical cylindrical column 920 mm. long and 38 mm. in diameter. The beaker is provided with a water-jacket. A jet 15 mm. long and 2 mm. in diameter at the top of the column points downwards along the axis of the column. The jet is connected through a pump and a heater to the bulk of the solution. The pump is set so that the solution can be circulated at a rate of 950 cc./min. from the bulk of the solution in the beaker through the pet onto the surface of the solution in the column. The column is inserted into the solution to such a depth that when the solution is being circulated the distance between the tip of the jet and the surface of the solution in the column is 710 mm.

To measure the foam height given by the nonionic synthetic detergent the solution is circulated and the temperature of the solution and of the water jacket are raised as follows:

Time (minutes):	Temperature ° C.
0	20
1	25
3	35
5	45
8	55
11	65

From 11 mins. onwards the temperature is kept constant. The height of the foam in the column is recorded.

With some nonionic synthetic detergents foam builds higher at the walls of the column than at the centre. The foam height at the centre can be judged easily by observing the agitation and size of the bubbles. In such a case the mean foam height at the wall and at the centre is recorded.

For the purposes of the definition of the term "nonionic foam depressant" the foam height for the nonionic synthetic detergent is the foam height recorded at 8 mins.

What is claimed is:

1. A non-ionic surfactant based detergent powder for use in a machine dishwasher consisting essentially of, by weight, from about 5% to about 30% of sodium metasilicate; from about 5% to about 30% of an oxidizing agent selected from the group consisting of chlorinated sodium orthophosphate, chlorinated isocyanurate and perborate; from about 25% to about 70% of a calicum-ion sequestrant selected from the group consisting of sodium tripolyphosphate, sodium nitrilotriacetate and tetrasodium ethylenediaminetetraacetate; and from about 0.5% to about 10% of a non-ionic surfactant mixture of:

(A) a condensation product of nonylphenol and 5 moles of ethylene oxide or a condensation product of random C_{11} to C_{15} secondary alcohol and ethylene oxide with an HLB value between 11.5 and 13.5; and

(B) a polyethyleneoxide-polypropyleneoxide condensate that consists of, by weight, between about 5% and about 15% polyethyleneoxide and between about 95% and about 85% polypropyleneoxide and has a molecular weight between about 1900 and about 2300;

the weight ratio of A to B being between about 1:2 and about 1:5.

2. A detergent powder as in claim **1** in which the powder contains between 40 and 65% of sodium tripolyphosphate, as calcium-ion sequestrant.

3. A detergent powder as in claim **1** containing from about 1% to about 5% of said non-ionic surfactant mixture.

4. A detergent powder as in claim **1** containing from 0.1 to 1% by weight of an anti-tarnishing agent.

References Cited

UNITED STATES PATENTS

2,829,102	4/1958	Ruff et al.	252—135
3,022,250	2/1962	Grifo et al.	252—135
3,248,330	4/1966	Feierstein et al.	252—135X

OTHER REFERENCES

"Tergitol" Nonionic 15-S-9, Union Carbide Chemicals Publication F-41151, August 1964, pp. 1, 2 and 6.

"Tergitol" S. Biodegradable Surfactants, Union Carbide Chemicals Publication F-41410, 1966, pp. 1-4, 6 and 15.

LEON D. ROSDOL, Primary Examiner

D. L. ALBRECHT, Assistant Examiner

U.S. Cl. X.R.

252—89, 135, 321, 358