Chlorine-Stable Machine Dishwashing Products

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Abstract

The increasing use of active chlorine-containing compounds in machine dishwashing has led to the need for chlorine-stable, low foaming detergent formulations. To avoid oxidative degradation of nonionic surfactant and simultaneous loss of available chlorine, a new basic formulation process has been devised. This obviates the need for modifying nonionic surfactants. The process requires a preferred order of addition and the use of tetrasodium pyrophosphate builder as an integral part of the composition. The detergent product is free-flowing, granular, readily soluble and exhibits no tendency to cake on storage. A suggested machine dishwashing formulation is given, and data are presented which show good chlorine stability and excellent dishwashing performance.

Introduction

THE HOME MACHINE DISHWASHER MARKET is growing at an ever increasing rate. Thus the sale of machines has risen from 295,000 in 1955 to 1,466,000 in 1967 (1), a fivefold increase in just 12 years. The total number of household machines currently in use in the United States is now reported to be greater than 10 million units (2), representing 18% of the country's 60 million electrically wired homes. Sanitarians, detergent compounders, fine china manufacturers, and makers of dishwashing machines are paying increased attention (3) to the effectiveness of machine dishwashing detergents. This interest has served to accentuate the need for an effective product that will satisfy the desires of everyone, especially those of Mrs. Average Housewife. In the formulation of machine dishwashing detergents, surface active agents are necessary to provide detergency, wetting, soil penetration, rinsing and drainage. A low foaming surfactant is needed to prevent the build-up of foam, which is aggravated by the presence of proteinaceous soils (4). As foaming increases, the speed of the dishwasher's spray arm decreases, resulting in decreased washing efficiency. The use of chlorinated trisodium phosphate or chlorinated cyanurates has found wide favor in machine dishwashing detergent products. Almost all of the products that are available on the supermarket shelves today contain an active chlorine-containing compound. The advantages of using active chlorine-containing compounds have been detailed (5). It has been reported (6) that, in addition to their germicidal action, they oxidize organic soils, some of which could otherwise foam excessively. The low foaming surfactants used in machine dishwashing detergents have been of the nonionic class, most generally block or heteric polymers of alkylene oxides or capped oxyethylated alkyl phenols (7). Manufacturers and compounders of nonionics, in an attempt to prevent oxidative degradation of their surfactants in contact with active chlorine-containing compounds, have resorted to various methods of modifying structures (8–12).

In the chemical interaction between many nonionic surfactants and active chlorine-containing compounds, the latter function as oxidizing agents and cause degradation of the surfactants during storage. The need to utilize proper formulating techniques when incorporating nonionic surfactants in detergent products containing active chlorine compounds has been recognized (6,8,13,14). Thus it is stated that when properly compounded the two can be used together to produce stable chlorine-containing nonionic based detergent formulations which will give low suds for use in machine dishwashing processes. However, no specific details are given and "properly compounded" means different things to different people.

Several methods have been reported for formulating machine dishwashing compounds based on both active chlorine-containing materials and nonionic surfactants. Only a few of the more pertinent will be referred to here. The Milenkovich and Henjum patent (16) describes a process in which an alkali metal silicate plus water are added to an anhydrous phosphate, together with a nonionic synthetic detergent. This is followed by adding chlorinated TSP, agitating and aging to obtain complete hydration, while maintaining rigid temperature control. The resulting product is characterized by remaining gel free in the detergent cup and is completely dissolved in the second rinse cycle. No mention is made of stability, or lack thereof, of the chlorinated TSP in products made by the teachings of this invention. In 1966, Podas and Crecelius reported (17) a method to produce a chlorine-stable machine dishwashing product by encapsulation of the nonionic in a separate step to protect it from the active chlorine-containing compound. However, no details were presented which would enable one to utilize this method. Further, no information was presented on the ratio of surfactant to available chlorine and no stability data were shown.

In the Oberle patent (18) some of these details are spelled out. A process for preparing a storage-stable detergent composition is claimed which comprises absorbing a liquid low foaming nonionic on one of several anhydrous carriers, such as $Na_5P_3O_{10}$ or Na_2CO_3, and then adding an aqueous solution of a phosphate to form an encapsulating coating. The mixture is then dried and blended with a chlorine-releasing agent. Storage stability data are given for a maximum of 170 days (almost 6 months); they reveal that only 13% of the original available chlorine is lost. The principal disadvantages to this process appear to be the need for encapsulating carrier particles containing absorbed nonionic surfactant, and a drying step.

A systematic study, undertaken with the primary objective of preparing stable active chlorine-containing detergents, has led to the development of a formulation process (15) which utilizes commonly encountered nonionic surfactants and does not require the use of specially capped, hydroxyl-free surfactants.

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[1] Presented at the AOCS-AACC Joint Meeting, Washington, D.C., April 1968.

TABLE I
Detergent Formulations Used in Testing Chlorine Stability

	Formulation, parts by weight						
Ingredients	1	2	3	4	6[b]	17	21
Na_2CO_3, reg. light	20	....	37.5	20	20	20	20
$Na_5P_3O_{10}$, anhydrous	35	....	17.5	....	....	....	....
$Na_4P_2O_7$, anhydrous	....	55	....	35	35	....	....
$Na_2B_4O_7$, anhydrous	....	....	....	....	....	....	35
Na_2SO_4, anhydrous	....	....	....	....	....	35	....
Nonionic[a], 40% aq. soln.	25	25	25	25	....	25	25
Water	....	....	....	....	25	....	....
Na_2SiO_3, pentahydrate	10	10	10	10	10	10	10
Chlorinated TSP	10	10	10	10	10	10	10
Starting available Cl, %	.39	.31	.32	.32	.33	.35	.33
% of Starting available Cl: after 130 days at 25 C	45	88	48	89	....	65	[c]

[a] Pluronic L-61, a polyoxyethylene-polyoxypropylene block copolymer.
[b] Control formulation.
[c] Not determined; product discolored in one day.

Methods

Preliminary stability tests indicate that some nonionic surfactants degrade upon coming in direct contact with sodium silicates or metasilicates as well as with active chlorine-containing compounds. A study was made on the effect of the sequence of addition of ingredients and the type of inorganic builder upon the stability of the product. By spraying an aqueous surfactant solution onto selected inorganic detergent builders in a rotating drum-type mixer, the materials agglomerated through partial hydration of the builders and simultaneous absorption of the surfactant. The agglomerated material was crushed and screened, and sodium metasilicate pentahydrate was added. After thorough mixing, the material became a dry, free-flowing granular product. Finally, the active chlorine-containing compound, either chlorinated trisodium phosphate or a chlorinated trisodium phosphate or a chlorinated cyanurate, was added and the product was thoroughly mixed and packaged. Available chlorine determinations were performed periodically using detergent formulations 1, 2, 3, 4 and 6, given in Table I. The nonionic surfactant was used at a 10% level rather than the 1–3% normally encountered in machine dishwashing compounds to accentuate any differences in degradation. Various proportions of inorganic builders were used to study their effects on chlorine stability. These tests were performed at an elevated temperature (50 C) to accelerate possible degradation and to obtain data in a relatively short time.

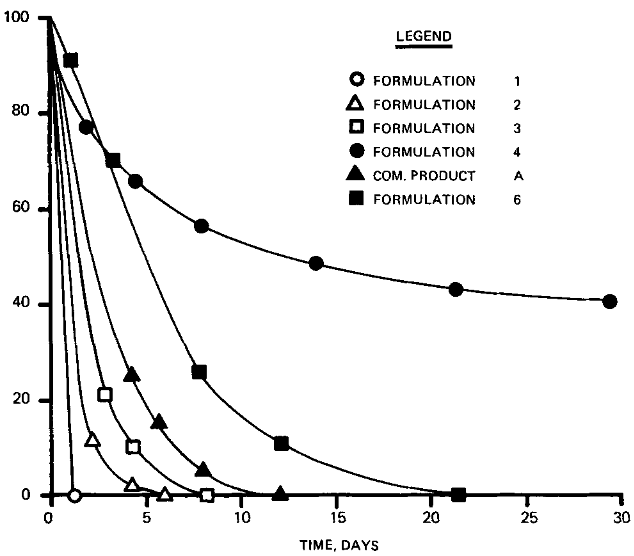

FIG. 1. Degradation curves at 50 C.

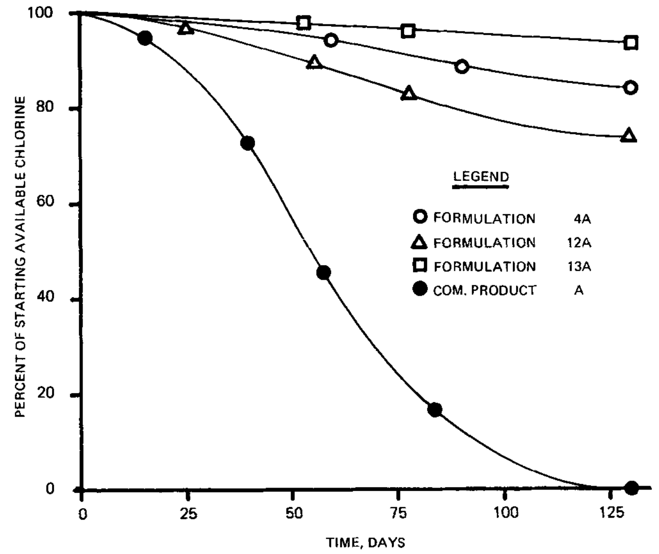

FIG. 2. Degradation curves at 25 C.

In Figure 1, the degradation curves, showing the decrease in per cent of initial available chlorine content, are plotted as a function of time. Commercial product A is included for comparison. These curves show formulation 4, containing 35% tetrasodium pyrophosphate, to be remarkably stable, indicating a smaller available chlorine loss than formulation 6, which contains no surfactant.

Another series of stability tests, using the same nonionic surfactant, were performed with various combinations of inorganic builders. These tests were made at room temperature storage conditions, over 130 days. The formulations were prepared as previously described. The outstanding stability of detergent formulations containing tetrasodium pyrophosphate was again demonstrated. The results, given in Table I, show that of the six formulations tested, only the ones containing 55% and 35% tetrasodium pyrophosphate retain 88% and 89%, respectively, of their starting available chlorine content. In the same period, the available chlorine contents of all other formulations decrease to the range of 45% to 65% of their starting values.

The mixing sequence used for preparing the formulations used in chlorine stability testing is the following: Add soda ash, tetrasodium pyrophosphate and sodium tripolyphosphate to a suitable mixer and mix; while mixing, spray or slowly pour the aqueous

TABLE II
Comparative Room Temperature Stabilities of Formulations Containing Various Surfactants

	% of Starting Available Chlorine Content					
	After 1 month		After 2 months		After 4 months	
Formulation[a]	Sprayed	Poured	Sprayed	Poured	Sprayed	Poured
4A	98	95	95	95	85	89
12A	96	92	84	85	74	75
13A	99	98	97	97	94	95

[a] 20% Na_2CO_3, 35% $Na_4P_2O_7$, 25% surfactant (40% aq. soln.), 10% SMS·5 H_2O, 10% chlorinated TSP. Surfactants used are:
4A—Pluronic L61 (Wyandotte Chemicals Corporation) a polyoxyethylene polyoxypropylene block copolymer.
12A—Plurafac RA-20 (Wyandotte Chemicals Corporation) an oxyalkylated fatty alcohol.
13A—Plurafac RA-30 (Wyandotte Chemicals Corporation) an oxyalkylated fatty alcohol.

TABLE III

Comparison of Chlorine Stabilities of Detergent Formulations Prepared by Various Methods

Method of Preparation	Chlorine Stability[a]	
(a) Addition of surfactant[b] solution after mixing all other ingredients	0%	in 8 days
(b) Same as (a) but adding chlorinated TSP after surfactant addition	32.7%	in 6 days
(c) Addition of $SMS \cdot 5\ H_2O$ and surfactant simultaneously	0%	in 5 days
(d) Using anhydrous sodium silicate instead of $SMS \cdot 5\ H_2O$	0%	in 6 days
(e) Recommended method	57% 38%	in 6 days and in 28 days

[a] Expressed as per cent of starting available chlorine content; samples were stored at 50 C.

[b] Pluronic L61, a polyoxyethylene polyoxypropylene block copolymer used in all tests.

solution of nonionic surfactant onto the mixture; with continued mixing, add sodium metasilicate pentahydrate; remove the mixture and screen; add active chlorine-containing compound and mix thoroughly; remove product from mixer and package in suitable container.

The effect of varying the active-containing compound was studied in a comparison of chlorinated trisodium phosphate with potassium dichloroisocyanurate, sodium dichloroisocyanurate and dichlorodimethyl hydantoin. The same nonionic was used with sodium sulfate added to compensate for the varying weights of the chlorine-containing component. During one month of testing at room temperature storage, the chlorine stability was practically the same for all compounds tested. Hence, for convenience, all subsequent tests were made with chlorinated trisodium phosphate as the active chlorine-containing compound.

Figure 2 shows room temperature degradation curves for three detergent formulations containing nonionic surfactants. Composition 4A contains a polyoxyethylene polyoxypropylene block copolymer, and 12A and 13A are based on oxyalkylated fatty alcohols. The degradation curve for room temperature storage of commercial product A, which had an initial available chlorine content of 0.47%, is included to show the difference in stability. Although the testing exceeded four months, the formulations still show remarkable stability, with no signs of discoloration or caking whatsoever.

A comparison of the room temperature degradation of the same three formulations prepared by simply pouring the nonionic solution versus spraying is given in Table II. The data show close agreement during four months. Hence, for practical purposes, no discernible differences are found in the chlorine stabilities of detergent formulations prepared by spraying or pouring the surfactant solution.

Comparative chlorine stability tests of detergent formulations prepared by some of the previously reported methods were performed. They demonstrate the necessity of preparing the detergent compositions according to our recommended sequence of admixing the ingredients. All samples, prepared by varying the sequence of admixing, have the following composition: 35% tetrasodium pyrophosphate, 20% sodium carbonate, 25% nonionic surfactant (a 40% aqueous solution), 10% sodium metasilicate pentahydrate and 10% chlorinated trisodium phosphate.

TABLE IV

Available Chlorine Contents of Household Machine Dishwashing Products

Commercial Products	Available Cl, %	
A	.50,	.47
B	.20,	.34
C	.48,	.70
D	.40,	.52
E	.35,	.28
F	.67,	.59
G	.19,	.23
H	.13,	.33

TABLE V

Chlorine Stability of Preferred Formulation

Time, Months	1	2	4	8	12	18
% of Starting Available Chlorine[a]	97	84	73	72	71	70

[a] 0.62%.

The techniques investigated were as follows: (a) addition of the aqueous solution of nonionic surfactant after mixing together all ingredients; (b) same as (a) but adding the chlorinated trisodium phosphate following addition of the surfactant; (c) adding metasilicate and surfactant simultaneously to the mixture of tetrasodium pyrophosphate and sodium carbonate and then adding the chlorinated trisodium phosphate; and (d) anhydrous sodium silicate powder instead of sodium metasilicate pentahydrate. The results of the storage tests at 50 C with these formulations are presented in Table III. The data show rapid degradation of all but the composition prepared by the recommended method. This formulation shows outstanding chlorine stability.

The importance of chlorine stability cannot be overemphasized. A number of commercial products are found to perform satisfactorily within a month or two of the date of production. However, some products are found to foam excessively after several months of storage at room temperature, due to rapidly decreasing available chlorine content and simultaneous degradation of the surfactant. Table IV shows the available chlorine contents of a number of commercial products which were purchased from supermarkets and analyzed immediately upon opening of the packages. The results vary from .13% to .70%, clearly indicating relatively short shelf life of some products tested. All samples were purchased in duplicate, at different times or at different supermarkets. Variations in active chlorine contents are noted. Commercial products A, C and D had 0% available chlorine after three months of storage at room temperature.

The composition of a preferred, chlorine-stable formulation, based on the teachings of this process (15), is the following: 35% TSPP, 25% STPP, 10% $SMS \cdot 5\ H_2O$, 10% nonionic surfactant (30% aqueous suspension of PLURAFAC RA-43, oxyalkylated fatty alcohol containing a protein soil defoamer) and 20% chlorinated TSP. The sequence of adding the materials is the same as previously described. The chlorine stability of this formulation over a period of 18 months of storage at room temperature is shown in Table V. The machine dishwashing performance of this formulation at the end of the test period is practically the same as that at the start,

TABLE VI

Comparative Foaming Effects of Machine Dishwashing Products

	Milk Soil		Egg Soil	
	Avg. Rpm[a]	Foam Ht., in.[b]	Avg. Rpm	Foam Ht., in.
Preferred Formulation				
Commercial Product	103	3/8	97	1/4
A	80	1–1/4	93	3/8
B	95	5/8	92	3/8
C	99	1/2	72	2–1/4
D	90	7/8	70	2–1/4

[a] Average spray arm speed of 2 and 4 min of wash cycle.

[b] At end of 4 min of wash cycle.

indicating negligible degradation of the surfactant during 18 months of storage. It is suggested that the high chlorine stability is achieved by absorption of the nonionic in the pyrophosphate, and simultaneous hydration of the latter with insufficient water to form the decahydrate, i.e., no more than 70% of theory.

The machine dishwashing performances of the preferred formulation versus four commercial products using milk and egg soil at 140 F, are given in Table VI. The test method is described elsewhere (4). Excellent foam control of the proteinaceous soils is demonstrated by the preferred formulation, which is also observed to dissolve rapidly. On the other hand, two of the four commercial products show undissolved granules remaining at the end of the wash cycle. Despite these differences, all the commercial products, as well as the preferred formulation, passed a standard food soil removal test (9).

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