Protein Soil Defoaming in Machine Dishwashers[1]

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Abstract

The machine washing of dishes that are heavily loaded with proteinaceous soil has been a problem facing consumers and the surfactant industry alike for many years. The rapid growth in the machine dishwasher market and the trend toward the use of lower water temperatures have tended to aggravate the resulting foaming problem for both the household and the industrial consumer of machine dishwashing detergents. Although many surfactants have been recommended for use in defoaming protein soils, no one product which satisfactorily defoams protein soils over a temperature range of 100–160F has been available.

A systematic study undertaken with the primary objective of defoaming egg and milk soils in machine dishwashers over wide temperature ranges has now led to the development of an effective protein soil defoaming system. This consists of monostearyl ester of phosphoric acid blended with special nonionic surfactants, in a mixture of alkaline builders, and provides excellent control of protein foam from 100–160F. Studies have been undertaken to show the effects of variations in monoalkyl ester concentration, types of surfactant, soil load, water temperature, water hardness and builder systems.

Introduction

THE GROWING ACCEPTANCE of machine dishwashers in the American home plus the increasing use of moderate temperatures in household hot water tanks due to lack of adequate capacity and the widespread emphasis on cold-water clothes washing detergents have created new requirements in machine dishwashing detergents. The machine manufacturers have not been idle either, modifying their machines to eliminate both the preheat and the purge cycle in order to do away with the resulting water waste.

All machine manufacturers, as well as formulators of machine dishwashing detergents, recommend a minimum water temperature of 140F. Recently reported (2) sanitizing studies using machine dishwashers in a U.S. Department of Agriculture Laboratory, were conducted at a temperature of 140F. Yet despite all published admonitions to the contrary, it is common knowledge that housewives frequently wash dishes at water temperatures as low as 100F, if not lower. The use of such low temperature water is often not deliberate, but is largely due to the presence of cool water in the line between the hot water tank and the machine.

The advantages of using a water temperature of 140F or higher are well known. There is less tendency for the nonionic surfactant present in the dishwashing detergent to foam. The development of excessive foam in the machine can result in overflow. Even moderate foam reduces the cleaning effectiveness of the machine's system. What is desirable is a minimum of foam. Any foam that does develop should be unstable and quick-breaking.

The problems encountered in household dishwashers are also found in industrial machines where generally higher temperatures are used. Although commercial establishments are supposed to wash dishes at 180F, or higher, it is not uncommon to encounter temperatures as low as 100F. The generally higher soil loads and spray arm pressures make effective defoaming at such low temperatures a prime requirement.

Although many different soils are found in both household and industrial machines, it has long been recognized (2,3) that proteinaceous foods cause the most difficulty in that they develop a tenacious, stable foam. It was the objective of this investigation to develop a surfactant system that would defoam protein soil under any conditions of machine dishwashing. This could be done in either one of two ways: a) find an additive that would be effective with several nonionic surfactants, or b) develop a surface active agent that would be effective without an additive. The work which will now be described encompasses only one aspect of the former approach. Additional data, encompassing other currently available systems, will be presented in another paper.

Experimental

Since the KitchenAid (Hobart Manufacturing Co.) dishwasher has been reported (4) to be effective for evaluating low-foaming mechanical dishwashing detergents, our test procedure is based on the use of the KitchenAid, Model KD-12P. The revolutions per minute (rpm) of the dishwasher's spray arm are reduced by foam and are a direct measure of the amount of foam generated. Where excessive foam develops, the foam not only overflows under the bottom seal of the door, but also slows the spray arm or stalls it completely.

In order to count the rpm's, the dishwashing machine was modified by installation of a mechanical counter. To observe the foam height inside the machine, a portion of the door was replaced with a transparent plastic window.

An 80-gallon capacity hot water heater was used solely for the dishwasher to maintain a constant temperature source. For tests requiring soft water, the tap water was passed through a water softener before being fed to the water heater. A Dole No. GS reducing valve was installed in the water line to the dishwasher to minimize or eliminate variations in line water pressure.

Since the control mechanism of the KitchenAid machine is a time-activated solenoid, it is desirable to keep the volume of water entering the machine constant by maintaining constant water pressure. An alternative method is to add an extra standard amount of water at the start of the wash cycle so that the excess water is drained out to a constant level.

The temperature of the inlet water was monitored by a thermometer in the line. A dial thermometer attached to the lower tray, just behind the plastic window in the door, indicated the water temperature in the machine. At the start, the machine was allowed to go through a few cycles to heat the inside to the desired temperature. The machine was started,

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TABLE I

Effect of No. of Carbon Atoms in Alkyl Chain on Defoaming of Egg Soil

No. of carbon atoms in alkyl chain	Alkyl ester (defoamer)	Average spray arm speed, rpm
2	Ethyl triethanolamine phosphate	<40
4	Monobutyl acid orthophosphate	>40 <70
5	Potassium salt of amyl phosphate	<40
8	Monoisooctyl acid orthophosphate	<40
8	Monooctyl acid orthophosphate	>40 <70
12	Monolauryl acid orthophosphate	>40 <70
12	High monolauryl acid orthophosphate	>40 <70
13	Monotridecyl acid orthophosphate	<40
16	Cetyl acid orthophosphate	>40 <70
18	Stearyl acid orthophosphate	≧75
18	Monooleyl acid orthophosphate	≧75
18	Monostearyl acid orthophosphate	≧75
18	High monostearyl acid orthophosphate	≧85

and following the purge cycle, the door was opened, automatically stopping the machine. Then 18.6 g of a detergent base, 0.3 g of a nonionic wetting agent, 0.05 g of an additive, and the protein soil, consisting of well-stirred whole egg or powdered milk, were placed inside the machine. The door was closed, automatically restarting the machine.

Once the washing cycle started, the counter was read and a stop watch started simultaneously. Readings on the counter were recorded after each of the first 4 min. The rpm's for the second and fourth minutes were averaged and recorded as the average spray arm speed. The controller was advanced to the exhaust cycle to discharge the contents. While the machine went through its normal two rinse cycles, the materials for the next test were prepared.

Results and Discussion

The operating conditions used in screening surfactants, additives, and combinations thereof for effectiveness in defoaming proteinaceous soils were as follows: tap water—7.0 ± 1.0 grains/gallon hardness; temperature—160F ± 5F for screening tests; 135F ± 5F for all subsequent tests; detergent base—18.6 g/wash cycle; composition of base—56% anhydrous sodium tripolyphosphate (STPP), 15% trisodium phosphate dodecahydrate (TSP · 12 H_2O), 20% anhydrous sodium metasilicate (SMS), 7% sodium sulfate (Na_2SO_4), 2% sodium chloride (NaCl); surfactant—0.3 g/wash cycle; additive—0.05 g/wash cycle; egg soil—15 ml stirred, raw whole egg/wash cycle.

Egg soil was selected for these tests because it is known to be more difficult to defoam than milk soil, as will be shown later. Many materials were examined but most of them failed to prevent the dishwasher from overflowing. A few examples of such ineffective materials were as follows: alkylphenoxy polyoxyethylene ethanol (9.5 EO); benzyl ether of oxyalkylated alkylphenol (9.5 EO); polyoxyethylene polyoxypropylene block copolymer (Pluronic F68); polyoxyethylene polyoxypropylene block copolymer (Pluronic L62); polyoxyethylene tall oil ester (23 EO); benzyl ether of oxyalkylated alkylphenol (9.5 EO) + 92% soap; Pluronic F68 + ethylene carbonate; Pluronic L62LF + octadecyl acid borate; Pluronic L62LF + nonyl acid borate; Pluronic L62LF + monotridecyl acid orthophosphate.

With water alone, the average spray arm speed was 100–110 rpm. However, under these egg soil defoaming conditions, an average spray arm speed of >75 rpm was considered very effective, >40 but <70 rpm considered partially effective, and <40 rpm considered ineffective.

TABLE II

Typical Analyses of MSAP Samples

	Percent by weight			
	High monoalkyl		Monoalkyl	
Sample no.	A	B	C	D
Composition				
Mono-ester	77.9	83.0	61.8	54.0
Di-ester	16.6	9.3	35.1	30.0
Free H_3PO_4 + unreacted stearyl alcohol	Bal.	Bal.	Bal.	Bal.

Some low-foaming nonionic surfactants were partially effective in the presence of egg soil. These surfactants as well as some others were slightly improved by the addition of various alkyl phosphate esters. Examples of such partially effective surfactants and surfactant-defoamer combinations included: polyoxyethylene polyoxypropylene block copolymer (Pluronic L61); polyoxyethylene polyoxypropylene block copolymer (Pluronic L62LF); polyoxyethylene polyoxypropylene heteric copolymer (Pluradot HA-430); oxyethylated ether of tallow alcohol (3 EO) + Pluronic L62LF; Pluronic L62LF + sodium di (2-ethylhexyl) phosphate; Pluronic L62LF + polyoxyethylene tall oil ester (23 EO); nonylphenoxy polyoxyethylene ethanol (9.5 EO) + monostearyl acid phosphate.

It was found (1) that a number of selected nonionic surfactants, when used with 18-carbon chain length alkyl phosphate esters as defoamers, gave exceptionally good performance in defoaming egg soil. One of the most effective was monostearyl acid phosphate, *hereinafter called MSAP.* The so-called alkyl phosphate esters are equimolar mixtures of monoalkyl and dialkyl esters. For the stearyl ester, these correspond to 37% and 63% by weight, respectively. A monostearyl ester is arbitrarily defined as having a monostearyl ester content of 50–70% by weight, while a high monostearyl ester, which is defined as containing >70% by weight of the monoester component, is referred to as high mono MSAP.

Examples of such surfactant-defoamer combinations included: Pluronic L62 + high mono MSAP; Pluronic L62 + MSAP; Pluronic L62LF + MSAP; Pluradot HA-430 + MSAP; Pluronic L62LF + monooleyl acid orthophosphate; benzyl ether of oxyalkylated alkylphenol (9.5 EO) + MSAP; Pluronic L62 + stearyl acid orthophosphate.

A study of the effect of varying the number of carbon atoms in the alkyl chain of phosphate esters on defoaming egg soil showed that the average spray arm speed did not increase proportionally with the number of carbon atoms. Excellent performance, however, was obtained with an 18-carbon alkyl chain length. A polyoxyethylene polyoxypropylene block copolymer (5) was used as the surfactant in these tests. The results are listed in Table I. It may be

TABLE III

Egg Soil Defoaming Effects of Pluronic L62 and MSAP

Materials	Weight, g	Spray arm speed, rpm
Detergent base	25.00	23
Detergent base	24.70	39
Pluronic L62	0.30	
Detergent base	24.70	59
MSAP	0.05	
Detergent base	24.70	81
Pluronic L62	0.30	
MSAP	0.05	

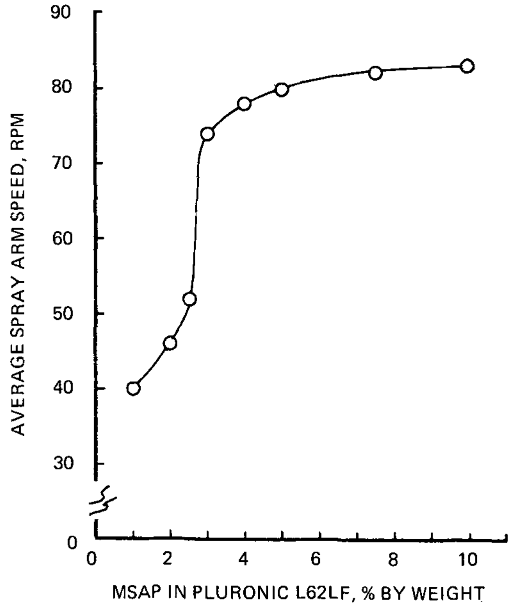

FIG. 1. Effect of MSAP concentration in defoaming egg soil.

noted that the high monostearyl ester performed much better than the monostearyl ester or the stearyl ester, indicating that the performance of these esters increased with an increase in the monoalkyl content. Typical analyses of some MSAP samples used in these studies are presented in Table II, which lists monoalkyl and dialkyl ester contents with the balance assumed to be free H_3PO_4 + unreacted stearyl alcohol.

Table III shows that a combination of a polyoxyethylene polyoxypropylene block copolymer and MSAP was synergistic in defoaming egg soil.

The effect of varying MSAP concentration in defoaming egg soil was determined at 135F ± 5F, holding all other conditions constant. The data, in Fig. 1, indicate that most of the defoaming effectiveness was accomplished by the addition of about 3% MSAP, with little further benefit at higher levels.

Similar tests were performed to compare two samples of MSAP, one a high monoalkyl and the other a monoalkyl ester. The results, given in Fig. 2, show the advantages of using a high mono MSAP. For example, the data show that 3% high mono was equivalent in defoaming action to 5% of the monoalkyl ester.

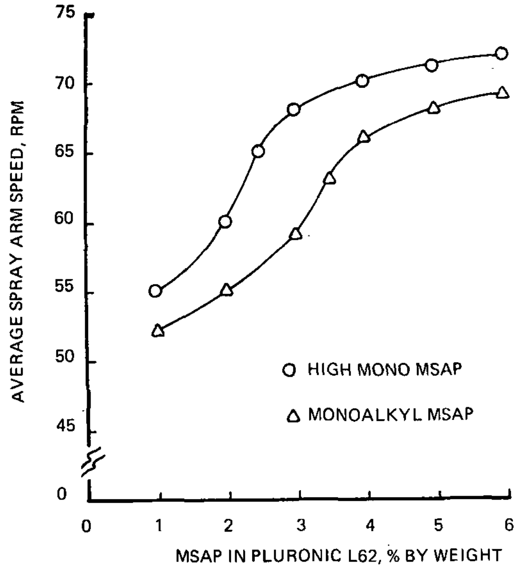

FIG. 2. Comparative effects of high mono and monoalkyl MSAP.

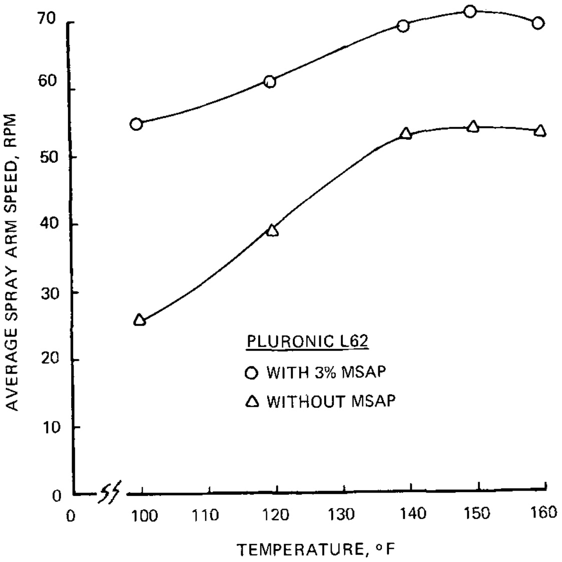

FIG. 3. Effect of temperature on egg soil foaming.

The effect of varying the operating temperature on the egg soil defoaming by a polyoxyethylene polyoxypropylene block copolymer, with and without addition of 3% MSAP, was determined over the range of 100F to 160F. As shown in Fig. 3, the defoaming action of MSAP was evident over the entire range studied. Even at 100F, the defoaming with 3% MSAP was equivalent to that without defoamer at 150F.

Similar comparative tests were performed at 135F ± 5F, with and without 3% MSAP addition to the surfactant, and adding varying amounts of egg soil. The results, presented in Fig. 4, showed that the amount of egg soil that can be defoamed without overflow was almost 15 ml with 3% MSAP, but less than a third of this amount without the defoamer.

The corresponding results obtained when using milk instead of egg are presented in Fig. 5. The lack of foam overflow over the entire milk soil range

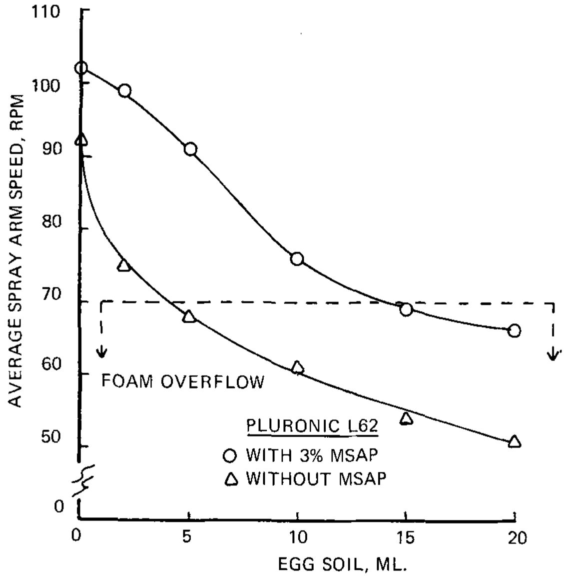

FIG. 4. Effect of egg soil concentration on foaming.

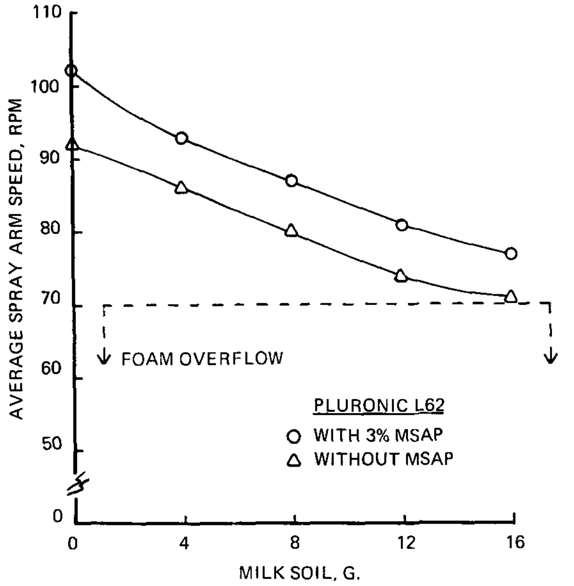

FIG. 5. Effect of milk soil concentration on foaming.

tested, with or without MSAP addition, indicated the relative ease in defoaming milk soil.

The foaming effect due to varying water hardness at four egg soil levels was investigated over the range of 0.5 grains/gallon to 32 grains/gallon. The data are plotted in Fig. 6 as a family of curves.

In the water hardness range of 10 grains to 32 grains there was a gradual drop in average spray arm speed for all four egg soil levels, as may be expected. However, in the soft water region, anomalies were obtained with the four soil levels behaving similarly. From the amount of tripolyphosphate added in the detergent base (Table I) and from the dishwasher capacity of 2⅓ gallons, the concentration of the tripolyphosphate was calculated as approximately 1.5 lb/100 gallons of wash water. It has been reported (6) that this concentration of tripolyphosphate at 60C (140F) sequesters water of 175 ppm $CaCO_3$ hardness. Since 175 ppm $CaCO_3$ corresponds to about 10 grains of water hardness, it is suggested that the anomalies in the curves at less than 10 grains may be attributed to the overly softened water.

Similar tests of water hardness versus four levels of milk soil produced results shown in Fig. 7, exhibiting anomalies in a family of curves resembling those obtained with egg soil. Because of the resemblance of the two families of curves, it appears that the foaming effect of the two proteinaceous soils is similar under the same conditions of testing.

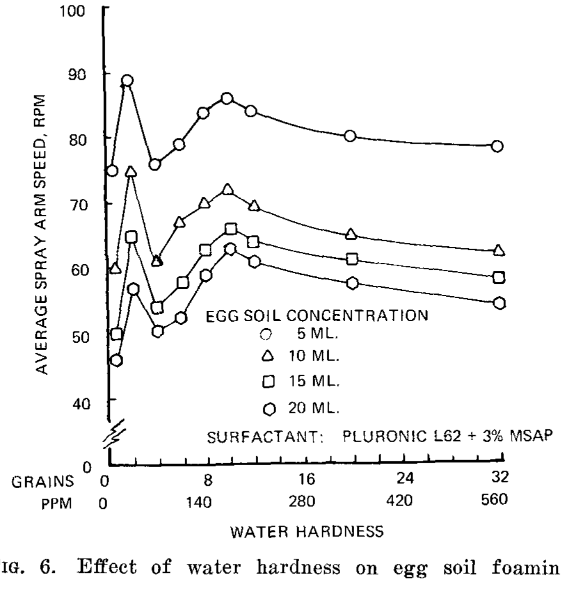

FIG. 6. Effect of water hardness on egg soil foaming.

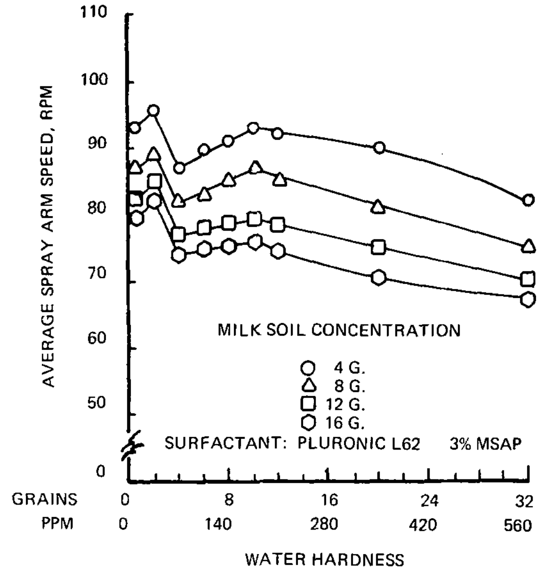

FIG. 7. Effect of water hardness on milk soil foaming.

The effect of variation in builder system upon egg soil defoaming was studied using a polyoxyethylene polyoxypropylene heteric copolymer (7) containing 3% MSAP. The inorganic builders were varied in the following ranges: soda ash 0–30%; total phosphates 30–71%; sodium metasilicate 10–30%; chlorinated TSP 0–20%; balance, sodium sulfate and/or sodium chloride 0–20%. The operating conditions and the compositions of five builder systems are presented in Table IV.

The results, presented in the same table, showed very little difference in average spray arm speed, indicating that within the variation in builder systems studied, negligible effects on changes in defoaming are observed.

TABLE IV
Effect of Builder System on Egg Soil Foaming[a]

Composition, % by weight	Builder system				
	A	B	C	D	E
Soda ash	0	30	20	10	0
STPP, anhydrous	56	30	20	10	35
TSP · 12 H_2O	15	0	30	20	0
TSPP, anhydrous	0	0	0	25	35
SMS, anhydrous	20	30	10	20	10
Sodium sulfate	7	10	20	5	0
Sodium chloride	2	0	0	0	0
Chlorinated TSP	0	0	0	10	20
Average spray arm speed, rpm	69	69	67	71	71

[a] Surfactant: Pluradot HA-430 + 3% MSAP.
Temperature: 135 ± 5F.

ACKNOWLEDGMENT

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