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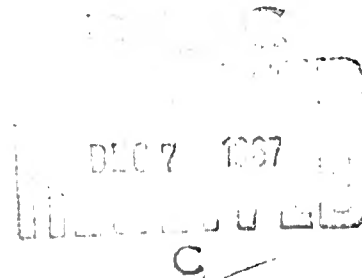
INTERIM REPORT

SUBSTITUTES FOR PHOSPHATES IN  
STEAM CLEANER P-C-437

BY

T. R. NICHOLS

DECEMBER 1967



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FINAL REPORT

SUBSTITUTES FOR PHOSPHATES IN STEAM CLEANER P-C-437

BY

T. R. MICHOLS

DECEMBER 1967

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DEPARTMENT OF THE ARMY PROJECT NO.  
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U. S. ARMY COATING AND CHEMICAL LABORATORY  
ABERDEEN PROVING GROUND  
MARYLAND

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## ABSTRACT

Anticipating a concerted effort to greatly reduce or eliminate phosphate in detergents and other cleaners, an initial study was made of the feasibility of substituting organic chelates for the phosphates in steam cleaners covered by Federal Specification P-C-437. Such an effort for phosphate elimination has recently been launched by industry (4).

This preliminary investigation indicates that phosphate-free compositions meeting P-C-437 requirements can be made by substituting for the phosphates various combinations of organic chelates with the incorporation of a hydrotrope.

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## I. INTRODUCTION

The need for replacing or partially replacing phosphates in detergents and other cleaners has been recognized in the past (1 - 3) and very recently (4). This is due to the fact that the growth of algae and other aquatic plants, that clog rivers and streams, is promoted by phosphates in the effluent from sewage treatment plants.

Objection has been raised to the use of nitrilotriacetic acid salt (NTA) as a substitute for phosphate, because NTA acts as a stimulant for algae growth (5). It has been shown, however, that such stimulation occurs only if  $PO_4$  and ammonia nitrogen are simultaneously present (6). Formulas described in this report completely substitute for phosphate, so that the objection to NTA or nitrogen containing chelates is avoided.

This initial report concerns the development of two compositions of phosphate-free steam cleaners which at this stage of development, have proved to be equal or superior to the standard comparison compound of Federal Specification P-C-437.

## II. DETAILS OF TEST

### A. Testing Procedure

Testing was conducted as prescribed in P-C-437. All tests were performed, with the exception of the fineness test and the one year caking in storage test, which are to be initiated soon.

### B. Phosphate Replacements

The composition of the P-C-437 standard comparison compound is:

Sodium metasilicate pentahydrate -----	35.0% by weight
Primary sodium phosphate monohydrate -----	10.5% by weight
Sodium tripolyphosphate -----	52.5% by weight
Nonionic surface active agent -----	2.0% by weight

The following compounds were used to replace the phosphates, keeping the concentrations of sodium metasilicate pentahydrate and nonionic surface active agents the same.

(1) Technical ethylenediamine tetraacetic acid tetrasodium salt dihydrate ( $EDTANa_4 \cdot 2H_2O$ ; one gram chelates 215 mg  $CaCO_3$ ).

(2) Technical nitrilotriacetic acid trisodium salt monohydrate ( $NTANa_3 \cdot H_2O$ ; one gram chelates 365-370 mg  $CaCO_3$ ).

- (3) U. S. P. citric acid anhydrous
- (4) Technical sodium acetate anhydrous
- (5) Alkyl naphthalene sodium sulfonate (Petro A. G. Special, 98% active)

### III. RESULTS AND DISCUSSION

Tables I and II give formulations of cleaners having varying pH values. In Table I, cleaner no. F has the pH value considered to be the most desirable. In Table II, cleaner no. 2 has the more desirable one. These two cleaners were selected for testing according to P-C-437.

From Table III, it is seen that each cleaner, no. F and no. 2, is superior in water softening to the standard comparison compound, their opalescent values being 0.005 while that for the standard comparison compound is 0.020.

In the other direct comparison test, namely cleaning efficiency, (Table III) each of the two cleaners, no. F and no. 2, is equal to or better than the standard comparison compound.

Each of the phosphate-free cleaners are well within the P-C-437 specification limits in the surface tension, penetration, aluminum corrosion, insolubles and free NaOH tests. The zero amount of free NaOH found is due to its neutralization by the citric acid incorporated in the formulations. Each of the cleaners also passes the rinsing and dusting tests.

In summary, these two cleaners, no. F and no. 2, were found to give results equal or superior to those given by the P-C-437 standard comparison compound.

### IV. REFERENCES

1. Pollution Fight Sells Chemicals. "Chemical and Engineering News," 44 (37) 18 (1966).
2. Fast Aeration Removes Phosphate From Sewage. "Chemical and Engineering News," 44 (13), 43 (1966).
3. Sawyer, Clair N., Problem of Phosphorous in Water Supplies. "American Water Works Association Journal," 57 (11), 1431-9 (1965).
4. Detergent Makers Agree to Seek Low Phosphate Products. "Chemical and Engineering News," 45 (33), 16 (1967).



5. Eutrophication and Detergents. "Soap and Chemical Specialties," XLIII (8), 37 (1967).

6. Shapiro, Joseph and Ribeiro, Roberto. Algal Growth and Sewage Effluent in the Potomac Estuary (Johns Hopkins Univ.) "Journal Water Pollution Control Federation," 37 (7) 1034-43 (1965).

APPENDIX A

TABLE I

COMPOSITIONS OF P-C-437 CLEANERS USING  $\text{NTANa}_3 \cdot \text{H}_2\text{O}$  AND THEIR pH VALUES

Composition, Percent by Weight

Cleaner	$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	$\text{NTANa}_3 \cdot \text{H}_2\text{O}$	Citric Acid Anhydrous	Sodium Acetate Anhydrous	Petro A G Special	Triton X 100	pH Value 0.5% Solution
A	35.0	40.0	5.0	--	18.0	2.0	11.50
B	35.0	40.0	9.0	--	14.0	2.0	11.15
C	35.0	40.0	8.0	15.0	--	2.0	11.30
D	35.0	45.0	7.5	10.5	--	2.0	11.35
E	35.0	45.0	7.5	--	10.5	2.0	11.35
F	35.0	40.0	8.5	9.5	5.0	2.0	11.25
P-C-437 requirement							10.50 - 11.40

TABLE II

COMPOSITIONS OF P-C-437 CLEANERS USING EDTANa<sub>4</sub>·2H<sub>2</sub>O AND THEIR pH VALUES

Cleaner	Composition, Percent by Weight							pH Value 0.5% Solution
	Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	EDTANa <sub>4</sub> ·2H <sub>2</sub> O	Citric Acid Anhydrous	Sodium Acetate Anhydrous	Petro A G Special	Triton X 100		
1	35.0	45.0	7.0	6.0	5.0	2.0	11.35	
2	35.0	45.0	8.0	6.0	4.0	2.0	11.20	

TABLE III

## RESULTS OF P-C-437 TESTS ON CLEANERS NOS. 2 AND F

Test	Cleaner No.		P-C-437 Requirement or Value Set by Standard Comparison Compound
	2	F	
Water softening, opalescence	0.005	0.005	0.020 max.
Cleaning efficiency, residue	2.0 mg	1.0 mg	2.1 mg max.
Free NaOH, milli- equivalents	zero	zero	0.02 max.
Insolubles	0.003%	0.005%	0.25% max.
Surface tension, dynes/cm	28.8	29.0	42.0 max.
Penetration	75-79	75-81	30.0 min.
Rinsing	Passes	Passes	Passes
Dusting	Passes	Passes	Passes
Aluminum corrosion, weight loss			
Al 1100			
0.25% solution	0.5 mg	0.6 mg	1.2 mg max.
1.20% solution	0.2 mg	0.2 mg	0.8 mg max.
Al 2024			
0.25% solution	0.4 mg	0.5 mg	0.8 mg max.
1.20% solution	0.2 mg	0.2 mg	0.5 mg max.

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