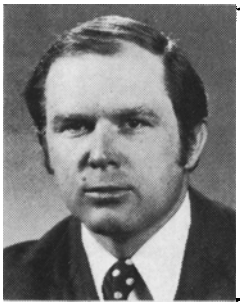

Organic Builders: A Review of Worldwide Efforts to Find Organic Replacements for Detergent Phosphates

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ABSTRACT

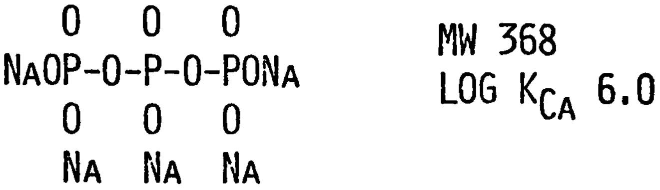
Continuing pressures to reduce phosphates in wastewaters have sustained an intensive worldwide search to develop acceptable substitutes. Organic polycarboxylate salts have been most extensively investigated because there are a large number of structural possibilities, and the possibility for biodegradation to innocuous CO_2 and H_2O offers an optimal answer to most environmental questions. In addition to testing known compounds, many novel structures have been synthesized in efforts to tailor materials with optimum properties. Stringent requirements for functional effectiveness, human safety, environmental acceptability, practical processability, and acceptable costs have limited the number of viable alternatives. Compounds that have been proposed are reviewed with particular attention to recent developments.

INTRODUCTION

Background

Continuing environmental, legal, and economic pressures to reduce the level of phosphates, particularly sodium tripolyphosphate (STPP) (Fig. 1), in detergents have for the past several years encouraged a worldwide search for suitable substitutes. This search has been active for more than a decade among the larger detergent manufacturers and their major chemical raw material suppliers. It was earlier thought that nitrilotriacetate (NTA) (Fig. 2) was a likely candidate to replace part if not all of the detergent phosphate. Commercial production of NTA in large quantities for detergent purposes was started in the U.S. only to be suddenly curtailed in December 1970, upon the recommendation of the U.S. Surgeon General, pending completion of further tests relating to its human and environmental safety. Since that time extensive testing has been conducted (1,2). In long term feeding studies weak carcinogenic effects in the urinary tracts of rats and mice fed continuously on very high levels of NTA acid or trisodium salt were found. (a) The significance of all the findings with respect to human safety has recently been assessed. (b) As of this writing (8-1-77), NTA is still under a voluntary ban in the U.S. but is being used in Canada at an average level of 15% in detergents as a partial STPP replacement.

While NTA research and controversy was active, the search for other organic substitutes for STPP continued and has been sustained for the past several years by both a



$$\begin{array}{c} O\quad O\quad O \\ NaOP\text{-}O\text{-}P\text{-}O\text{-}PONa \\ O\quad O\quad O \\ Na\quad Na\quad Na \end{array}$$

FIG. 1. Pentasodium tripolyphosphate (STPP).

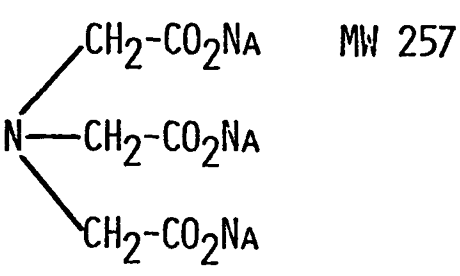


FIG. 2. Trisodium nitrilotriacetate (NTA Na_3).

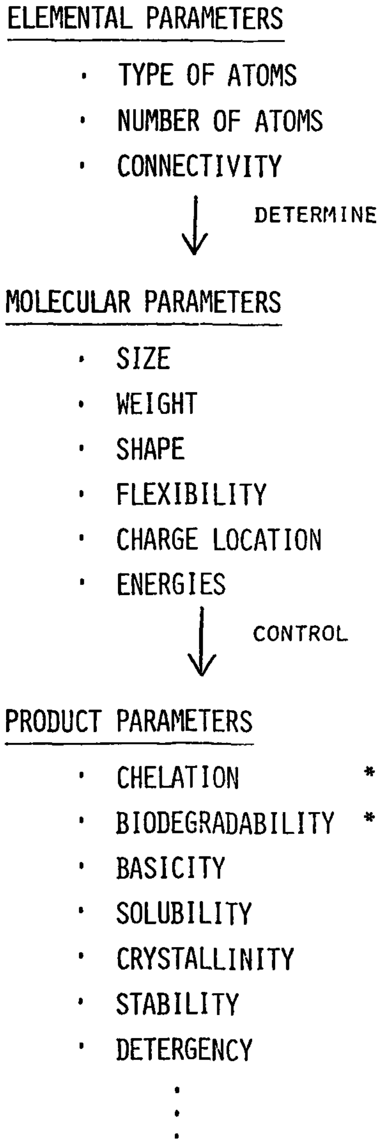


FIG. 3. Structure determines functionality.

$$M^{+2} + L^{-N} \rightleftharpoons ML^{2-N}$$

$$K_M = \frac{[ML^{2-N}]}{[M^{+2}][L^{-N}]}$$

$$(M^{+2} = Ca^{+2} \text{ OR } Mg^{+2})$$

FIG. 4. Stability constant.

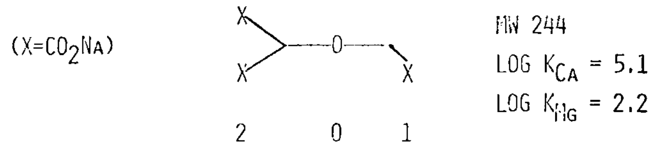


FIG. 5. 2-Oxa-1,1,3-propanetricarboxylate (carboxymethyltartronate, CMT).

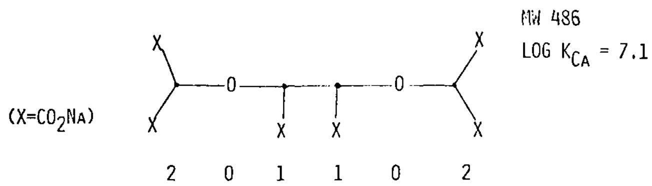


FIG. 6. 2-Oxa-1,3,4-butanetricarboxylate (carboxymethyloxysuccinate, CMOS).

broader number of participants and a greater intensity of effort, as evidenced by the high level of recent worldwide patent activity concerned with various organic compounds for this use (3-8).

Why Organic Builders?

The number of practical elemental building blocks for detergent materials is really rather limited. In the periodic table there is already at least some degree of environmental concern with B and N as well as P. Of the remaining abundant elements capable of acting as a structural backbone, carbon offers the largest number of easily achieved connectivity possibilities with which to tailor variable and hopefully acceptable molecular and product parameters (Fig. 3). In attempting to mimic the various desirable properties of STPP, its chelating properties for Ca^{++} and Mg^{++} are probably the most indispensible and least easily replaced by other substances. For this reason chelating properties of organic polycarboxylates, in the form of their sodium salts, have been most intensively investigated.

The various structural possibilities are astronomically large and include small as well as macromolecules. Many show chelating properties. Some, particularly certain members of the family of ether carboxylates, have calcium binding strengths, as measured by the familiar stability constant, K_m, (Fig. 4) comparing favorably with STPP and NTA. Of these, a somewhat smaller number are susceptible to biodegradation by acclimated bacteria inhabiting sewage systems and natural waters to produce, as ultimate waste products, water and carbon dioxide. Both of these wastes are innocuous and compatible with the environment without producing undue stresses on receiving bodies of water. Moreover, rapid biodegradation eliminates the need to answer many other difficult and expensive-to-answer questions that must be raised, and ultimately answered, about the long term environmental effects of sewering large quantities of any persistent, nondegradable, insoluble, or recalcitrant materials, whether organic or inorganic. Rapid and complete biodegradability therefore offers what can be considered an optimal answer to further environmental impact questions. Not all organic builder candidates, even if based only on C, H, and O, are able to demonstrate the desired biodegradability characteristics, but the fraction that can has provided justification for continued intensive scrutiny of this large class of possible materials.

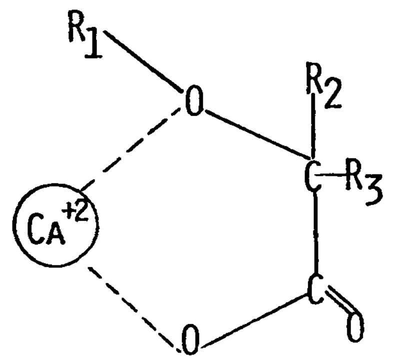


FIG. 7. α-Ether carboxylate groups coordinate to calcium ion.

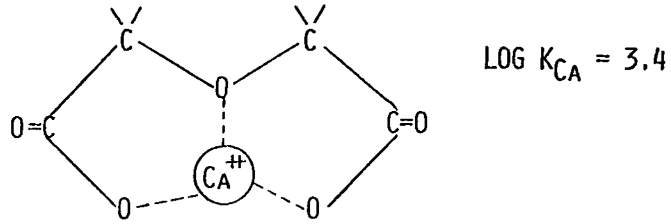


FIG. 8. Oxydiacetate – Ca^{++} complex (16).

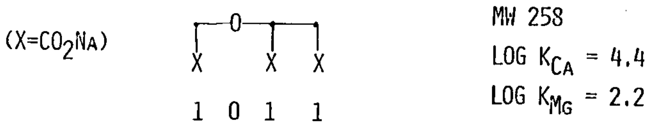


FIG. 9. 2,5-Dioxa-1,1,3,4,6,6-hexanehexacarboxylate (TMD) (18).

STATE OF THE ART: LOW MOLECULAR WEIGHT ETHER CARBOXYLATES

The subject of organic builder salts as replacements for sodium tripolyphosphate was previously reviewed by Matzner, Crutchfield, Langguth, and Swisher in 1973 (9,10). Many different general classes of compounds and specific structures including NTA analogs, which had been considered up to that time, were discussed. Screening criteria and tests used in the selection of potential candidates were described. A good correlation between sequestering power for Ca^{++} and Mg^{++} and resulting detergency performance was demonstrated. Comparative data were shown for a number of promising new organic candidates that were incompletely identified but that were mostly novel ether carboxylates, a relatively unexplored but large family of compounds that seems to offer many of the desired properties and that utilizes only the elements C, H, and O plus Na as building blocks. Identification of specific candidates for serious commercial developmental effort was at that time still pending.

Since then carboxymethyltartronate (CMT) (Fig. 5) has been selected as one model product and has been further developed by Monsanto as a potential commercial candidate (11).

A similar compound, carboxymethyloxysuccinate

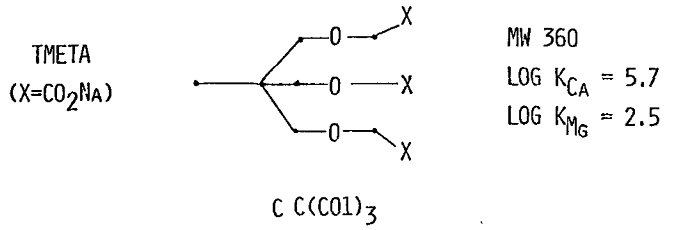


FIG. 10. 1,1,1-Tris(carboxymethoxymethyl)ethane (21).

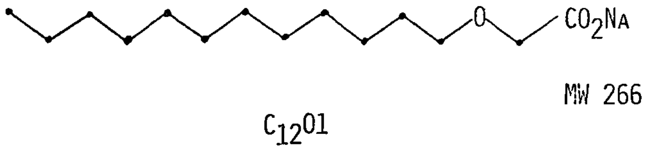


FIG. 11. Dodecyloxyacetate (DOA).

(CMOS), (Fig. 6) originally developed at Lever Brothers Company (12,13) has also received attention as another potential commercial candidate and is reported to be under development by others (14).

These two products both have in common an ether carboxylate moiety in which at least one ether oxygen and one or more carboxylate groups attached to the alpha carbons can simultaneously act as coordinating sites for calcium ion (Fig. 7).

Many possibilities exist for substitution at R_1, R_2, and R_3 with other oxygen and/or carboxylate-containing groups that are essential to insure adequate strength of binding by formation of polydentate structures. With oxydiacetate (ODA) (15) for example, the structure of the aqueous complex has been proved (16) to be as illustrated in Figure 8.

The log K_{Ca} value of 3.4 for this complex (17) is too low for good builder effectiveness, as is the case with citrate. As the number of sterically well-positioned binding sites increases further, the strength of binding also increases, which is favorable for detergency; but molecular weight simultaneously increases, which in turn decreases the weight efficiency of the builder.

A trade-off is thus required between strength or intensity of binding and capacity or efficiency of binding. It is not readily obvious what the optimum structure will be, particularly when unpredictable biodegradation requirements are included. Divalent electrode titrations (9) provide one simple experimental means for evaluating relative efficiency of small quantities of various structures for metal ion binding. A large number of possible ether carboxylate structures has now been synthesized and comparatively evaluated by our labs as well as by others (18,19). Correlations between structure and performance based on results reported by others as well as on previously unreported work of our own are now becoming more apparent and will be reviewed.

Recent Advances

Kemper and co-workers (18) reported log K_{Ca} values for a series of 17 ether carboxylates, including both CMT and CMOS, and showed a reasonable correlation between log K_{Ca} values and washing efficiency relative to STPP when

TABLE I

Calcium and Magnesium Binding by Ether Carboxylates

Structure	Bio test	Log K_{Ca}	Log K_{Mg}	Log K_{Ca}/K_{Mg}	Detergency as % of STPP
C2O2		7.2	5.7	1.5	101
OC2O2CO		7.0	6.3	0.7	89
┌C2O2C┐	*[a]	7.0	5.5	1.6	107
C2O2C		6.7	5.4	1.3	107
1O11O1		6.5	3.1	3.4	73
CC2O1		6.3	4.1	2.2	108
OC2O1	*	6.3	3.6	2.7	96
2O2		6.1	3.8	2.3	88
2OϕO2		6.1	2.2	3.9	78
C2O1	*	6.0	4.0	2.0	100
2O1CC		5.8	2.8	3.0	83
CCO2O1	*	5.8	2.7	3.1	76
1O2O1		5.8	2.8	3.0	86
C2OCO2C		5.7	3.2	2.5	87
2OCCO2		5.7 (5.7)[b]	2.9	2.8	78
C2O1C		5.5	3.8	1.7	97
OC2O1C		5.5	2.6	2.9	84
11O11		5.5	4.6	0.9	93
1O2OCCOCCO2O1		5.4	2.4	3.0	70
2O1C	*	5.3	2.7	3.6	90
OC2O1C (75%)		5.3	2.6	2.7	84
CO2O1	*	5.3	1.7	3.6	78
┌11O11┐		5.3 (5.8)	3.8	1.5	85
2O11		5.1	4.7	0.4	95
1O11OC		5.1	1.8	3.3	—
1O11O		5.1 (5.0)	1.2	3.8	—
2O1 CMT	*	5.0 (5.1)	2.2	2.8	87
2O1OC		5.0	1.7	3.3	76
1O111		4.9	3.1	1.8	—
C2OCO2C		4.8	1.3	3.5	71
C2Oϕ-X		4.4	2.8	1.6	—
1O11 CMOS	*	4.3 (4.4)	2.2	2.1	—
C1O11		4.0	1.3	2.7	77
1O1O1		3.6	1.1	2.5	—
1O1		3.4	<1	>3	64
C1O1C		2.0	<1	>2	—
2CCOCC2		<2	<1	~1	57

[a] Showed good removal in activated sludge tests. Selected for further evaluations.
[b] Log K_{Ca} values in parentheses are from Ref. 18.

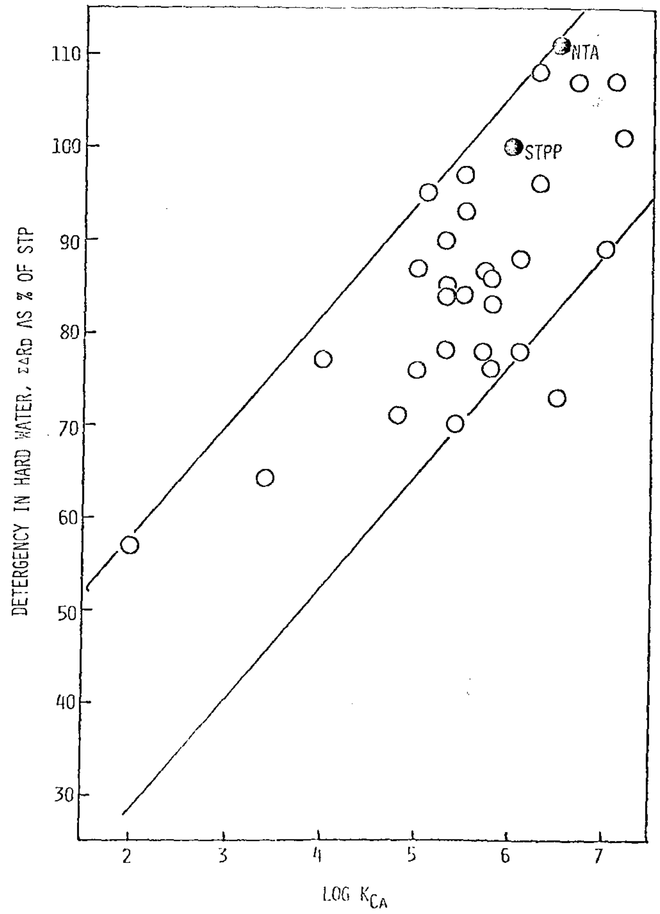


FIG. 12. Detergency vs. K_{Ca}.

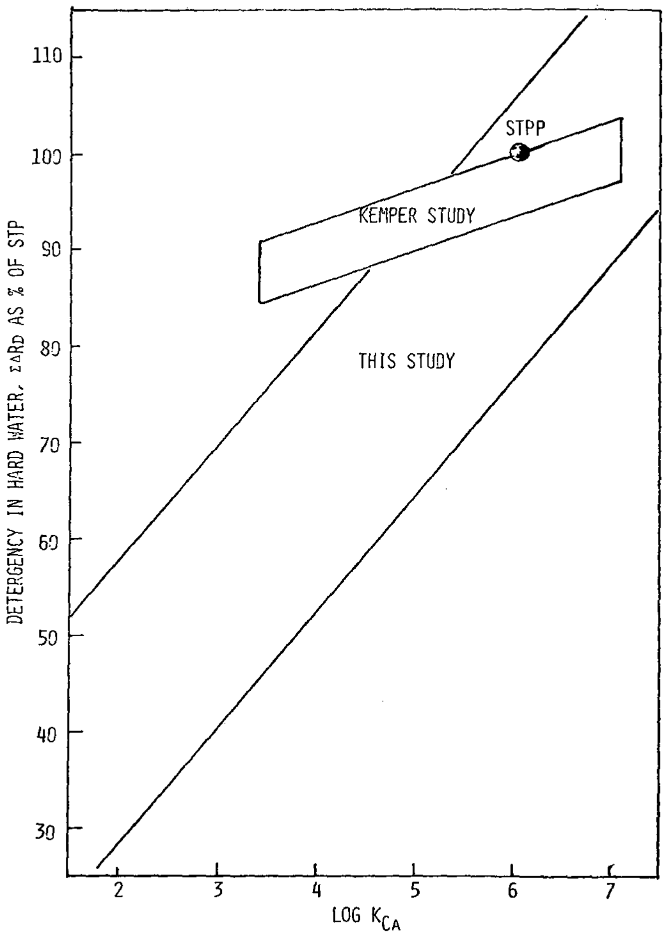


FIG. 13. Comparison of Monsanto and Kemper studies.

the builders were used in equimolar quantities. They also studied biodegradability. Both their results and our studies indicate that due to its lower molecular weight and higher K_{Ca} value, CMT has a slight advantage over CMOS with respect to weight efficiency for functional builder performance. This has been further confirmed by the work of Brouwer and co-workers at Unilever (19). CMOS, on the other hand, has a slight advantage over CMT with respect to ease of biodegradation. Biodegradation of CMT has been separately studied in greater depth (20). The results indicate that both compounds will be degraded in full-scale activated sludge waste treatment plants.

The highest performing ether structure in the Kemper study (18) was 2,5-dioxa-1,1,3,4,6,6-hexanehexacarboxylate (Fig. 9) which gave a favorable log K_{Ca} value of 7.1 compared to 6.0 for STPP and 6.5 for NTA. It is interesting to note that this structure is formally equivalent to two molecules of CMT joined together via a carbon-carbon bond between the CH_2 groups of the acetate moiety. It was reported in preliminary screening tests to be not readily biodegraded, however.

Abe and Matsumura (21) in Japan have very recently reviewed physicochemical properties of 38 carboxylate builders, mostly ether carboxylates, including some mono, di, tri, tetra, and penta carboxylates. The best performing chelating type builder from that study was 1,1,1-tris-(carboxymethoxymethyl)ethane (Fig. 10) which was also the structure from their series with the highest value for log K_{Ca}. The reported value of 5.7 is close to that for STPP. Its biodegradation was not studied. They also report that good detergency results were obtained when dodecyloxyacetate (Fig. 11), a nonchelating ether monocarboxylate structure, was substituted for STPP. Structures such as this are probably best considered for classification purposes as surfactants rather than as builders since they lower surface tension and form micelles in the fashion of conventional surfactants. Increasing the level of surfactant to compensate for performance losses resulting from STPP removal represents one of several alternatives to replacement of STPP by an organic builder. This and other alternatives will be considered further in the concluding section of this paper. For the present we will confine further consideration only to chelating-type builders which form soluble 1:1 (metal to ligand) or higher complexes with Ca^{++} and Mg^{++} with particular emphasis on the ether carboxylates.

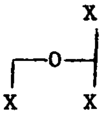
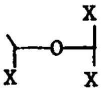
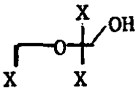
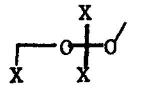
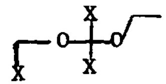
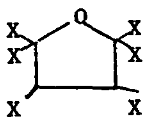
We have now screened over 600 samples of candidate materials of all types. Approximately 40 of these showed sequestration performance $\geqslant$70% of STPP on the previously described (9) divalent electrode test, and of these, the majority were novel ether carboxylate structures synthesized in our lab specifically for this purpose.

Table I summarizes previously unpublished data on a series of 38 ether carboxylates that we have synthesized and compared. Values for log K_{Ca} and log K_{Mg} were estimated from divalent ion electrode titrations. Detergency values for synthetic sebum/airborne particulate soil were measured in Terg-o-tometer tests in hard water (200 ppm as $CaCO_3$; Ca/Mg=3/2) for three builder levels (25%, 37.5%, 50%) on two fabrics (cotton and 65/35 PE/cotton blend) using 0.15% of a standard formulation with 17% LAS as the surfactant. Results shown are the sum of reflectance increases in the six tests as a percentage of similar STPP performance.

Five structures were common to both the Kemper studies (18) and our own. Comparison of log K_{Ca} values estimated by the different methods show good agreement, to within 0.1 log unit for four of the five. Overlap with the ether carboxylate compounds of the Abe study (21) includes only one compound in common (oxydiacetate) on

TABLE II

Comparison of Selected Ether Carboxylates

Structure ($X=CO_2Na$)	Biodegradation activated sludge	Sequestration % of STPP	Detergency, % of STPP			
			Hardwater screening test	Extended tests		
				Cot.	PE/C	
 (CMT)	Good	89	87	95 100	105 116	Hot Cold
	Good	85	90	98 99	110 117	
	Good	103	96	99 98	106 98	
	Good	70	78	91 92	100 106	
	Good	74	76	94 102	101 116	
	Erratic	135	107	101 102	97 105	
	Poor	144-200	127	117 119	125 130	
NTA	Good	152	110	102 110	108 113	
STPP	--	100	100	100 100	100 100	

which there is also close agreement with known K_{Ca} values (17). The structural formulas for the individual ether carboxylates in Table I are given in a simple abbreviated notation in which backbone atoms are listed in order with C=carbon, O=oxygen, $1{=}-\overset{|}{\underset{|}{C}}CO_2Na$, $2{=}-\overset{|}{C}(CO_2Na)_2$, $\emptyset=C_6H_4$, $X=CO_2Na$, and H's understood at all other unspecified bonding sties. The structures are listed in order of descending log K_{Ca} values. Four compounds had log K_{Ca} values of about 7. Differences in specificity for Ca^{++} and Mg^{++} are apparent from the value of $\log \frac{K_{Ca}}{K_{Mg}} = (\log K_{Ca} - \log K_{Mg})$. Higher values correspond to strong Ca^{++} preference. For log K_{Ca}/K_{Mg} values >3, Ca^{++} is preferred over Mg^{+2} by a factor of 10^3 or more. If Ca^{++} is more detrimental to detergency than Mg^{++}, as suggested by the relative solubility of calcium and magnesium salts of many surfactants, then preferential binding of Ca^{++} before Mg^{++} should be desirable for best deployment of builder in situations of builder underuse or excessive water hardness. On the other hand, in the presence of excess builder, overall performance will be maximized when Ca^{++} and Mg^{++} are both tightly bound.

The data from Table I are plotted in Figure 12 which shows detergency as a function of log K_{Ca}. A clear correlation is evident despite considerable scatter. All of the data with the exception of a single point (structure 101101) fit neatly between parallel lines which slightly exceed estimated 98% confidence limits for reproducibility of the performance data. If the correlation band from this study is overlaid with the corresponding band from the Kemper study (18) (Fig. 13) a difference in slope can be expected from differences in test procedures. A difference in the widths of the bands can reflect different precision measurements, and/or the equalizing effect of their using equimolar amounts, while we used equal weight amounts in testing.

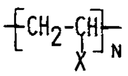
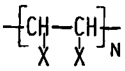
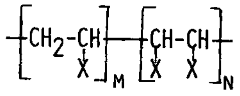
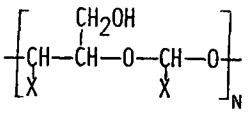
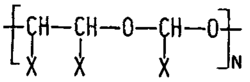
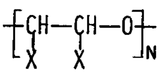
A number of structures in this study show chelation values and detergency performance exceeding CMOS and CMT. Some of these compounds were also found to be biodegradable in activated sludge screening tests. Several that showed evidence of some degree of biodegradability have received further evaluations and additional data for these are shown in Table II.

Additional detergency evaluations including tests in hot and cold water, on two fabrics, over a wide range of water hardness values showed that all of the compounds from a simple detergency building standpoint have adequate functionality to replace STPP. Ease of the biodegradation varies considerably with the better performers generally requiring longer acclimation times and showing more tendencies toward erratic degradation under some conditions. From the combined standpoints of performance, biodegradability, and potential routes for commercial manufacture, none at this time seems to be a clearly superior candidate to CMT.

TABLE III

Representative Polymeric Carboxylate Structures[a]

$(X=CO_2NA)$

Raw materials		Polymers
1. Acrylic acid	$\xrightarrow{\text{Polymerize}}$	 $\left[CH_2-\underset{X}{CH}\right]_N$
2. Maleic anhydride	$\xrightarrow{\text{Polymerize}}$	 $\left[\underset{X}{CH}-\underset{X}{CH}\right]_N$
3. Acrylic acid + maleic anhydride	$\xrightarrow{\text{Copolymerize}}$	 $\left[CH_2-\underset{X}{CH}\right]_M\left[\underset{X}{CH}-\underset{X}{CH}\right]_N$
4. Starch	$\xrightarrow{\text{Oxidize}}$	 $\left[\underset{X}{CH}-\overset{CH_2OH}{CH}-O-\underset{X}{CH}-O\right]_N$
5. Alginic acid	$\xrightarrow{\text{Oxidize}}$	 $\left[\underset{X}{CH}-\underset{X}{CH}-O-\underset{X}{CH}-O\right]_N$
6. Epoxysuccinate	$\longrightarrow$	 $\left[\underset{X}{CH}-\underset{X}{CH}-O\right]_N$

[a]Performance is best for large N. Biodegradation is best for small N.

Some generalizations regarding optimization of chemical structures for the family of low molecular weight ether carboxylates that have evolved during all these evaluations can be made. They are not without exception, but indicate observed trends, other things being equal.

For strong, efficient Ca^{++} binding:

1. Log $K_{Ca} \geqslant 5$ is desired with minimum molecular weight.
2. Carboxylate and ether oxygens on α carbons are the best ligand groups.
3. Ether oxygens are better than ketal oxygens.
4. Substituted malonate groups>malonate>succinate>acetate>propionate.
5. Total anionic charge >2 but <5, unless 2:1 or higher complexes form.
6. Close steric fit of at least four donor oxygens around Ca^{++} ion is possible with space-filling molecular models (CPK).
7. A minimum number of degrees of freedom in the backbone reduces unfavorable conformational possibilities.

For ready biodegradation:

1. Predictive power is poor, no rules are certain.
2. Single experiments are not definitive.
3. Minor, seemingly insignificant, differences in structure can have major influence on bio properties.
4. Anions of lower charge tend to degrade better than higher.
5. Anions of smaller K_{Ca} value degrade better than larger.
6. Some molecules degrade without acclimation.
7. Some molecules require prior acclimation.
8. Some molecules do not appear to degrade under any conditions, even after extensive acclimation.

STATE OF THE ART: POLYMERS

Polymeric polyelectrolytes have long been recognized as functionally excellent builder materials (22). Functional performance twice as effective as that of STPP on a weight basis has been demonstrated. Copolymers based on maleic anhydride as a basic raw material were seriously investigated in our labs in the late 1960s. We in fact had developed a copolymer of maleic anhydride and acrylic acid, as the sodium salt, to the point of initial pilot plant production of samples. Development work was terminated when it was conclusively demonstrated with C^{14} labeling studies that the polymer was disappearing in sewage treatment tests by adsorption onto the sludge and not by degradation to CO_2 (23). This type of product has recently been reproposed by Canadian researchers (24) who questioned the need for biodegradation.

There appear to be two divergent viewpoints with respect to the environmental acceptability of polymeric carboxylate builders based on carbon-carbon backbones. There does seem to be general agreement that such polymers as a class show excellent performance but rather poor biodegradability. A more liberal view suggests that simple removal, perhaps by adsorption on sewage sludge, without biodegradation to CO_2, may be a satisfactory and acceptable fate. A more conservative viewpoint maintains that accumulation with possible concentration somewhere in the environment would be an undesirable but inevitable result of widespread sewage disposal of nondegradable organic materials. Because of the large quantities anticipated for a successful STPP replacement (in the U.S. up to a million tons per year), proof of environmental safety for accumulating, nondegradable materials would seem to be a never-ending task of constantly escalating proportions. Acceptance of a truly biodegradable polymer seems possible, while acceptance of a poorly or partly degradable one is at best highly problematic. Methods for studying the biodegradability of organic materials including polymeric builders have recently been reviewed (25).

Table III summarizes several representative types of polymeric carboxylates that show good builder performance. Chain length and charge density seem to be the critical structural properties with longer chains and higher charge densities being preferred. Performance equivalent to STPP requires a minimum charge density of about one anionic charge per two backbone atoms. Performance exceeding STPP on a weight basis by a factor of up to two is observed for charge densities approaching one unit of anionic charge per backbone atom.

Polymers can coil back on themselves in solution as they form complexes with Ca^{++} creating low energy intramolecular binding sites which are probably less dependent on specific molecular geometry than the specific binding sites of lower molecular weight compounds. Thus, specific polymer structure is less important to functionality. Some polymers have been described as being biodegradable. Carboxylated starches derived from natural polymer sources have shown some degree of degradation but are much slower than underivatized starch.

One of the more interesting synthetic polymer candidates is a product based on an alpha hydroxyacrylate backbone which is being developed by Solvay (26). Recent preliminary biodegradation tests of a material of this structure in our labs showed 12 ± 10% theoretical CO_2 evolution in 28 days. Lower molecular weight ether carboxylates such as CMT and CMOS show 80-90% in the same test (27).

The best present polymeric builder candidates have outstanding detergency performance, but problematic biodegradation. Their future, relative to lower molecular weight materials would seem to be dependent upon their limits for biodegradability and relative cost/efficiency, which both remain to be defined. They could be economically attractive compared to STPP at up to two times the price per unit weight, provided the biodegradability problem can be adequately resolved without harming performance.

COSTS

When cost is considered, present organic builder candidates which are acceptable on the basis of both performance and biodegradability screening appear hard-pressed on the basis of presently projected raw materials, processing, and investment costs to offer sufficient economic incentive for immediate development as replacements for STPP. This is, of course, subject to rapid reversal by further technical advances in the development of low cost, high yield processes. There seems to be no truly fundamental technical barrier which would prevent a superior-performing, readily biodegradable, cost-competitive organic builder from eventually being developed. Research in this direction seems, therefore, likely to continue.

ALTERNATIVES

Some other alternatives to STPP replacement have been recently reviewed by Berth et al. (28). Let us reexamine some of the other alternatives to the use of organic builders:

1. The need for reduction of phosphates in detergents would be obviated by widespread installation of adequate sewage treatment facilities to remove effluent phosphates from all sources, including human wastes as well as detergent sources. This seems likely to occur in populous regions over the long term. It has already occurred in some locations. The expected timetable is slow. Existing legislation that bans or limits detergent phosphates in some populous locations and that is pending in others must be complied with.

2. A competitive nonorganic replacement for STPP could be adopted. Zeolites (29) are receiving serious evaluation and can functionally replace at least part of the role of STPP since they can bind Ca^{++} tightly. Zeolites have certain deficiencies: very weak magnesium binding, an equivalent weight for strong calcium binding which is significantly inferior to the best organic candidates, and slower kinetics for binding. Some of the long term consequences of the use of insolubles in detergents also remain questionable. Use of adjunct organic builders in conjunction with zeolites can augment their performance. Thus, zeolites may limit but do not necessarily eliminate a role for organic builders in detergents.

3. Development of new, builderless detergent formulations, based on surfactant systems which are less sensitive to calcium and magnesium ions would also reduce but not eliminate the need for builders. Even if surfactant precipitation is prevented, the need to overwhelm the strong Ca^{++}-soil interactions remains. Chelating builders are inherently more efficient on a weight basis at this task than either surfactants or zeolites. The same conclusion holds for the alternative of simply increasing the level of present surfactants. The true value of an organic builder in a phosphate-free formulation may well be thought of in terms of the excess surfactant that it can replace, rather than in terms of the equivalent STPP that has been legislatively displaced.

4. The high solubility and aqueous stability of some ether carboxylates makes them attractive for use in built liquid formulations, a use for which STPP has never been practical because the hydrolytic stability and solubility limits of STPP are not well suited for such use. Tetrapotassium pyrophosphate (TKPP), which has been widely used as a builder in liquid detergent formulations, is functionally replaceable by highly soluble organic builders. Because of relative costs, organic builders could become economically feasible in liquid formulations before they do in solid formulations.

ACKNOWLEDGMENTS

The invaluable collaborations of K.P. Lannert, J.N. Rapko, R.D. Harken, and C.J. Upton with novel product syntheses; R.D. Swisher and W.E. Gledhill with biodegradation testing; R.P. Langguth and L.W. Mecey with detergency evaluations; L.A. Highfill with metal ion titrations; as well as the advice and encouragement of C.F. Callis, E.A. Matzner, and P.A. Tierney are all gratefully acknowledged.

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