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Phosphate-free Detergents

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Phosphate-free Detergents*

by

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Summary

Samples of seven brands of nominally phosphate-free laundry detergents were purchased during October, 1970. These were analysed for the ecologically undesirable ingredients: phosphate, borate, nitrilotriacetate (NTA), and anionic surfactant (cleaning agent). Sears, Lemon Low Suds No. 311, and Concern detergents were essentially free of these ingredients. Basic-L and Topco detergents contained small amounts of anionic surfactants but did not contain the other ingredients listed above. Ecolo-G contained both traces of phosphate (0.2-0.4%) and small amounts of anionic surfactants. Cold Water All (Liquid) contained NTA, which has been found by the National Institutes of Environmental Health Sciences to cause birth defects in rats and mice under special conditions.

In addition, the detergents were analysed for nitrogen, silicate, carbonate, pH, sodium chloride, water, brighteners, alcohol-soluble materials, and grams of detergent per wash. Every detergent contained sodium silicate, a corrosion inhibitor and water softener, and brighteners. Ecolo-G contained 42-48% sodium chloride, an inert filler. Concern contained 82% water, which is appreciably more than other liquid laundry detergents.

Granular detergents contained large amounts of carbonates and were quite alkaline. The pH at washing concentrations ranged from 10.7 (Basic-L) to 11.3 (Ecolo-G), which is substantially more alkaline than typical phosphate-based detergents. For Basic-L, Ecolo-G, and Topco detergents the pH increases appreciably as the concentration is increased. Avoidance of excessive contact of skin with concentrated solutions of detergents will prevent possible skin irritation from the silicates and high pH of these detergents. Adequate rinsing will minimize possible fabric deterioration from residues of these alkaline detergents.

R.C.S.I. feels that the ultimate benefit to the area's lakes and streams from a reduction in phosphate input is worth any minor changes in washday procedures necessary to use these phosphate-free detergents to their best advantage.

1. Composition of Laundry Detergents

The principal active ingredients in laundry detergents are surfactants, builders (water softening agents) and corrosion inhibitors. Minor ingredients include foam boosters, redeposition preventatives, brighteners, dyes, and perfumes. Inert compounds may be present as fillers. Enzymes are present in a number of detergents as aids in cleaning and stain removal. The composition of a typical heavy-duty laundry detergent is given in Table I.

*In this report "detergent" is used to refer to the complete cleaning formulation.

Table I

Typical Heavy-Duty Granular-Detergent Formulation (1)

Material	Percent by wt.	Purpose
Sodium dodecylbenzene-sulfonate (LAS)	18	Anionic surfactant
Sodium xylene sulfonate	3	Dedusting agent
Diethanolamide of coconut fatty acids	3	Foam booster
Sodium tripolyphosphate	50	Improves cleaning power (builder)
Sodium silicate	6	Anticorrosion agent
Carboxymethylcellulose	0.5	Soil redeposition preventative
Optical brightener	0.3	Fluorescent whitener
Benzotriazole	0.1	Antitarnishing agent
Other inorganic salts and water	19.1	Fillers
	100.0	

Surfactants. Surfactants, the cleaning agents, may be of several general types: anionic, nonionic, or cationic. Most detergents contain anionic surfactants, principally linear alkylbenzenesulfonate (LAS). LAS is moderately biodegradable under aerobic conditions, but is not biodegraded under anaerobic conditions. Other common types of anionic detergents are alcohol sulfates (also present in toothpastes), alkanesulfonates and alkenylsulfonates. Nonionic surfactants, such as sucrose esters or ethoxylated alcohols, are generally more expensive than LAS. However, they are effective cleaners, more easily biodegraded, and may be less sensitive to hardness ions than anionic surfactants. Cationic surfactants are generally less effective and too expensive for use in laundry detergents.

Builders. The major component in detergents is usually the builder, which assists the cleaning action of the surfactant. The required properties of a builder are 1. to soften water by tying up hardness ions such as calcium, magnesium and iron either by chelation or precipitation, 2. to help emulsify oil and grease, 3. to control the alkalinity of the water, and 4. to help keep dirt particles in suspension.

Polyphosphates are the principal builders in detergents at present. Triphosphate is the most common type of polyphosphate used, but tetraphosphates and longer-chain polyphosphates, commonly called "hexametaphosphate", are also used. Polyphosphates soften water by chelation and provide moderate alkalinity. Chelation is the binding of ions in a soluble, inactive form which does not interfere with cleaning action. Orthophosphates are used in some detergents, principally for controlling alkalinity rather than for their water softening properties.

Sodium carbonate (washing soda) was commonly used for water softening before phosphates and synthetic detergents came into general use. Carbonates remove hardness ions by precipitating them in granular form. Sodium carbonate is considerably more alkaline than polyphosphates.

Sodium tetraborate (Borax) has been used for many years as a water softening agent. The toxicity of borate is discussed below.

Nitrilotriacetate (NTA) is an effective chelating agent which has been used in detergents in the United States since 1967. However, because of the findings of birth defects in test animals, as discussed below, Proctor and Gamble announced that NTA will be discontinued from its products.

Organic polyelectrolytes containing only carbon, hydrogen, oxygen and sometimes nitrogen are effective water softening agents. Biodegradability varies for these polyelectrolytes, but readily biodegradable materials can be made.

Sodium citrate is a water softening agent of limited effectiveness which is present in a few detergents. It is a constituent of all living cells and can be rapidly biodegraded to carbon dioxide and water.

When used in sufficient quantity, sodium silicate softens water by precipitating silicates of hardness ions. Sodium silicate is present in almost all detergents to act as an anticorrosion agent. Most silicates are strongly alkaline.

2. Phosphate-free Detergents

In response to consumer demands for detergents with lower phosphate contents, a number of detergents not relying on phosphate builders have come onto the market, principally during the fall of 1970. In Table III are given results of analyses for various constituents in seven detergents which are advertised as being phosphate-free. A minus sign indicates that the constituent is below the limit of detection of the analytical method. The consequences of the presence of these ingredients are discussed in the appendix.

Table II

Name	Manufacturer	Cost[a] per wash[b]
Basic L	Shaklee Products	$.073
Cold Water All (liquid)	Lever Bros.	.104
Concern	Ladco Chemical Products	.086
Ecolo-G	North American Chemical Co.	.069
Lemon Low Suds No. 311	Dist. by McCrory Bros.	.101
Sears	DeSoto	.066
Topco	Topco Associates	.044

[a] Retail price not including taxes

[b] Recommended quantity for top-loading washer

Table III

Composition of Phosphate-free Detergents

Detergent	Basic-L	Cold Water All (Liq)	Concern	Ecolo-G, Oct.	Ecolo-G, Nov.	Lemon Low Suds No. 311	Sears	Topco
Form	Gran	Liq	Liq	Gran	Gran	Gran	Gran	Gran
Phosphate, $\%PO_4$	<.1	<.1	<.1	0.4	0.2	<.1	<.1	<.1
Nitrogen, %N	<.1	1.0	0.3	0.1	0.1	0.5	0.1	<.1
NTA, $\%Na_3C_6H_6NO_6$	-	18	-	-	-	-	-	-
pH at washing concentrations	10.7	10.3	9.4	11.2	11.3	10.8	10.8	11.1
pH at 1% in distilled water	11.7	11.0	10.2	11.9	11.9	11.2	11.1	11.8
Carbonate, $\%Na_2CO_3$	73	-	-	21	15	71	64	62
Silicate, $\%Na_2SiO_3 \cdot 3H_2O$	7	14	1	17	14	11	12	15
Borate	-	-	-	-	-	-	-	-
Methylene blue active substances, % Dodecylbenzenesulfonate	2.1	-	-	1.0	1.3	-	-	0.8
Alcohol-soluble material, %	12	13	16	7	8	9	11	13
Brightener	+	+	+	+	+	+	+	+
Water insoluble material	-	-	-	+	+	-	-	-
Salt, % NaCl	-	-	-	42	48	-	-	-
Water, $\% H_2O$	5	56	82	9	13	7	10	14
Amount per load, g	50	150	120	180	190	120	120	120

3. Use of Phosphate-free Detergents

No attempt was made to evaluate the cleaning effectiveness of the detergents analysed in this study. Consumer Bulletin (2) has rated the cleaning power of three phosphate-free detergents, of which two are included in this study. Sears detergent was rated as very good in hot hard water and poor in cold soft water; the overall rating was "intermediate". Ecolo-G was rated as fair in hot hard water and poor in cold water, both hard and soft; it received the overall rating of "not recommended". The tap water of the City of Rochester has a hardness of 5 to 7 grains per gallon (85 to 120 mg/l $CaCO_3$); the county water has a hardness of 7 grains per gallon. These waters are hard, although not as hard as most tapwater in the heartland of the United States. Good cleaning results are to be expected from the use in hot water of Sears detergent and probably certain others of the detergents of this study.

In general, the total weight of surfactant per washload is considerably less for these detergents than that for typical phosphate-based detergents. Poor cleaning will not necessarily result, however, since the amount of surfactant in phosphate-based detergents may be more than adequate. Furthermore the surfactant used in most phosphate-based detergents is of a different type from that used in phosphate-free detergents and may be less effective.

The granular detergents utilize a different water softening principle from that utilized by phosphate-based detergents; thus, changes in washday habits may result in improved performance from them. These detergents rely on precipitation rather than chelation of hardness ions. For this reason R.C.S.I. suggests that you try adding the detergent to the wash water before the clothes are added. This will allow the precipitated hardness salts to settle to the bottom of the washer and may make it less likely that they will be deposited on the clothes.

The granular detergents are strongly alkaline and may cause skin irritation. Furthermore, the pH values of Basic-L, Ecolo-G and Topco detergents increase rapidly as the concentration is increased. For these reasons one should avoid skin contact with concentrated solutions of these detergents. If collars and cuffs are to be scrubbed by hand, either protective gloves should be worn or other detergents or soaps should be used for this purpose. Alkaline residues on clothing can cause fabric deterioration (3). Thus, the amount of water used during the rinse cycle should never be reduced. In some cases an additional rinsing cycle may be desirable to remove final traces of alkaline residues. R.C.S.I. feels that any minor changes in washday habits needed to use phosphate-free detergents to their best advantage are warranted by the potential benefit to the area's waters.

Cold Water All contained NTA as a builder and can be used in the same manner as phosphate-based detergents. However, it is expected that most detergents containing NTA will ultimately be removed from the market (see Appendix).

Changes in Formulation. The formulations of the detergents of this study may be subject to change at any time. It was observed that Ecolo-G purchased during November was of distinctly different appearance from that sold earlier. Analysis of this batch (Table III) indicated that it contained the same ingredients in generally similar proportions to that previously sold. Thus the difference in appearance is due to variations in manufacture and not to a reformulation of this product.

TECHNICAL APPENDIX

1. Phosphates and Arsenic

Previous R.C.S.I. bulletins (4) have listed the phosphate contents of a number of detergents and have discussed the harmful effect of phosphates upon streams and lakes. It has been estimated that 70% of the phosphate in Lake Erie and 57% of the phosphate in Lake Ontario comes from detergents (5). Rochester is the largest single source of phosphates discharging into Lake Ontario. The presence of arsenic in phosphate-based detergents has been cited as a possible ecological hazard. Arsenic occurs naturally in phosphate ores and is incorporated into phosphate-based detergents at concentrations of 10-70 ppm (5). The amount of arsenic in sewage arising from detergents can be estimated as 1-2 ppb, which does not constitute a significant health hazard.

Small but distinctly non-zero values for phosphate were obtained for Ecolo-G; these were reproducible and do not appear to be artifacts of the analytical method. All detergents in this study contain less than 0.5% phosphate; thus, there is negligible contribution of phosphates to waste waters from the use of these detergents.

2. Nitrogen

Nitrogen is present in amounts greater than 0.1% in Cold Water All, Concern and Lemon Low Suds No. 311. Nitrogen is essential to plant growth and is possibly the limiting nutrient for growth of algae in Irondequoit Bay (6). However, the amount introduced by detergents is small relative to that already present in sewage. It is estimated that if all detergents were based in part on nitrogen-containing builders (NTA), the nitrogen content of municipal sewage would be increased by only 5%.

The nitrogen in these detergents could come from foam stabilizers, NTA or other nitrogen-containing builders such as aminocarboxylates, or enzymes. However, the enzymes used in detergents do not function effectively at the high pH values typical for these detergents and are probably absent.

3. NTA

Nitrilotriacetate (NTA) is a strong chelating agent, 1.4 to 1.8 times as effective as triphosphate on a weight basis. NTA has been used for several years in Sweden to replace phosphates in some detergents. Detergents containing NTA were introduced in the United States in 1967. Proctor and Gamble had planned to replace 38% of the phosphates in detergents with NTA by 1972.

The safety of NTA has been questioned by a number of researchers. An article on NTA based on testimony before the Senate Subcommittee on Air and Water Pollution, Committee of Public Works, was published in the September, 1970, issue of Environment (7). There are five questions which have been raised about the consequences of large scale use of NTA: a. direct toxic effects; b. transport of heavy metals in the environment by chelation; c. possible formation of carcinogenic compounds during sewage treatment; d. adequacy of breakdown of NTA during sewage treatment; and e. stimulation of plant growth by nitrates produced during breakdown of NTA.

More extensive use of NTA has been banned in Sweden pending evaluation of its toxicological effects. In recent studies by the National Institute of Environmental Health Sciences it was found that high rates of fetal injuries to rats and mice occurred when NTA was administered along with cadmium and methylmercury compounds (8). The high rate of embryo toxicity and congenital abnormalities observed was not found when the metals were administered alone. The Environmental Protection Agency and Surgeon General of the PHS have recommended that "NTA detergent products not be used in certain limited areas which have both well water supplies and septic tanks and in which these treatment systems are operating under completely anaerobic conditions and where short-circuiting of septic tank effluent directly into well supplies is occurring." Because of the stigma of the Surgeon General's statement, Proctor and Gamble is phasing out the use of NTA in its products.

Of the detergents in this study, only Cold Water All contains significant amounts of NTA.

4. <u>Borates</u>

Sodium tetraborate (Borax) has been used for many years as a water softening agent. It is present in approximately one fourth of phosphate-based detergents, generally constituting about 10% of the detergent, when present. Borax is sold in pure form and in combination with other builders as a water softening agent. Borax has been advertised as a solution to the problem of pollution arising from detergents. It has been reported (9) that borates are used in the phosphate-free detergent sold by Montgomery Ward.

All forms of boron are toxic, except those which are very insoluble. Borates and boric acid are classified as moderately toxic (10) to man. The fatal dose of boric acid for adults is 5-30 g, and poisoning occurs from ingestion of 2-5 g of boric acid (ca. 1 tsp.). Borates are not readily absorbed through intact skin, but rapid absorption occurs through cut, burned, or abraded skin; severe poisoning can result from absorption of rather small amounts of borates. Borates are accumulated in the body especially in the liver and body fat; chronic exposure results in borism, characterized by dry skin, eruptions and gastric disturbances.

It is often believed that boric acid and borates are good antiseptics and should be used for washing of diapers and infants' clothing. However, borates are effective generally only against fungi, and even a saturated solution (4%) of boric acid does not kill pathogenic bacteria (11). Thus, boric acid and borates are at best feeble antiseptics.

Borates are also toxic to plants, and are used in some herbicides. The optimum concentration of borates in water for plants is about 0.5 mg/l (as boron); much less than this may stunt growth and more than this may cause harmful effects. As little as 1 mg/l boron can be harmful to sensitive plants; 1 to 2 mg/l in saturated extracts of soil is considered high for land plants. Water plants are somewhat more tolerant of borates. Photosynthesis in valisneria (a water plant) is inhibited by borax at concentrations of 6 to 60 mg/l as boron (12). Use of solutions of borax in forest fire fighting has been found to cause inhibition of seed germination and high mortality of seedlings for at least a year after application (13).

The present concentrations of borates in waste waters are approaching the toxic limits for some plants. Borates in municipal wastes have been found to be about 1-2 mg/l as boron (14); this has limited the use of such wastes for irrigation and fertilization to boron-resistant crops. In Russia river waters have been found to contain 0.03 to 2 mg/l of boron (15).

Thus, borates do not appear to be a satisfactory general substitute for phosphates in detergents. There is a potential health hazard to users upon skin contact. An appreciable increase in the use of borates might also cause damage to boron-sensitive plants which come into contact with waste waters.

Of the detergents in this study, none contains measurable amounts of borates.

5. pH

pH is the measure of the acidity or alkalinity of water. A value of 7 corresponds to neutral conditions. The pH scale is logarithmic, which means that an increase of one unit corresponds to a tenfold increase in effective concentration of alkali. An increase of 0.3 units corresponds to an increase of a factor of two in effective concentration of alkali. The pH of four typical phosphate-based detergents was found to average 10.2, which can be considered moderately alkaline.

The pH values of solutions of the detergents of this study are rather sensitive to concentration. This effect is most pronounced with Basic-L, Ecolo-G, and Topco detergents. This means that if concentrated solutions are employed, the pH will be much higher than the values given in Table III, and any adverse effects of alkalinity will be magnified. The pH of solutions of the granular detergents averaged about 10.9 at normal washing concentrations and 11.5 at a concentration of 1%.

The pH of most of the phosphate-free detergents can be considered rather alkaline. Highly alkaline substances can cause skin irritation for some people. Furthermore, if residues of alkaline detergents are left in clothing by inadequate rinsing, significant fabric deterioration can occur. The avoidance of this possible problem is discussed under "Use of Phosphate-free Detergents."

The pH of the granular detergents is established by the presence of sodium silicate and sodium carbonate. Sodium carbonate is the principal ingredient of Basic-L, Lemon Low Suds No. 311, Sears, and Topco detergents.

6. Silicates

Silicates are present in almost all detergents as corrosion inhibitors. Except for Basic-L and Concern, the detergents examined in this study contain considerably more silicates than the typical laundry detergent of Table I.

Although sodium silicate can be made (3) in a form suitable for use at moderate alkalinities (less than pH 10), the usual form of crystalline sodium metasilicate is suitable only for use under strongly alkaline conditions (at about pH 11). Contact with strongly alkaline silicates has been found to cause dermatitis in some individuals (16). A number of cases of skin irritation and skin rashes have been reported by people using certain of the detergents of this study. This undesirable side effect can be minimized by the techniques discussed under "Use of Phosphate-free Detergents".

7. Methylene Blue-Active Substances

The methylene blue analysis measures anionic detergents without distinguishing between the various types. Prior to 1965 branched-chain alkylbenzenesulfonate (ABS) was the most commonly used surfactant. ABS is not easily biodegradable and persists in the environment for long periods. In 1965 ABS was replaced by linear alkylbenzenesulfonate (LAS), which is more easily biodegradable under aerobic conditions. LAS is not degraded under anaerobic conditions. LAS is more toxic to fish than ABS, but because it is more rapidly biodegraded, it causes fewer problems.

In Suffolk County, Long Island, drinking water supplies have become contaminated by undegraded surfactants arising from entry of home wastes into ground waters via septic tank systems or cesspools. The Suffolk County Legislature has responded to this problem by passing legislation aimed at prohibiting use of detergents containing surfactants which are not easily biodegradable. The law prohibits the sale, after March 1, 1971, of detergents containing linear alkylbenzenesulfonates and other methylene blue-active substances. Most detergents on the market are included in this ban.

Of the detergents tested, Basic-L, Ecolo-G and Topco detergents contain 1-2% MBA substances (as dodecylbenzenesulfonate). These amounts are small compared to typical phosphate-based detergents. Xylenesulfonate, an anionic surfactant used as a dedusting agent in some laundry detergents, can be distinguished from alkylbenzenesulfonates on the basis of its insolubility in ether. Ether-insoluble surfactants are essentially absent from all detergents in this study. Analysis of a mixture of several phosphate-based detergents indicated an average of 21% MBA substances, which is in agreement with the value given in Table I for a typical heavy duty laundry detergent.

8. Ethanol-soluble Materials

The ethanol-soluble fraction of detergents is essentially a measure of the organic material present. The inorganic builders, NTA, and sodium citrate are practically insoluble in ethanol. Surfactants are generally soluble in ethanol, as are foam stabilizers, and brighteners. The amount of ethanol soluble material per wash load varies from 6 g for Basic-L to 20 g for Cold Water All.

9. Sodium Chloride

Sodium chloride (table salt) was found to be present only in Ecolo-G, in which it is the principal constituent. The results of this study are in accord with the reported (17) criticism that Ecolo-G consists of 45% sodium chloride. It is used as an inert filler of very low cost (less than $0.02 per pound). Although the presence of salt in large quantities is harmful to plants, the use of sodium chloride as a filler in detergents does not result in significant environmental damage. If all detergents were replaced by Ecolo-G, the chloride content of municipal sewage would be increased by approximately 15 mg/l, which is less than one fifth of the normal values for municipal sewage. Furthermore, the amount of salt used to de-ice roads in winter is much larger than that which would be introduced if all detergents contained large amounts of sodium chloride.

10. Water

None of the granular detergents of this study contains water in appreciable excess of what is expected from normal water of hydration of the builders employed. Liquid detergents generally contain sufficient water to dissolve the inorganic materials present and to provide a product of convenient fluidity. Cold Water All contains 56% water, which results in a rather thick formulation. Concern contains 82% water and is quite fluid. It was found that at least half of the water could be removed (to give a final composition of 67% water) without impairing the ease of pouring Concern.

11. Methods

Samples of phosphate-free detergents were purchased during October, 1970. A second sample of Ecolo-G was purchased in November.

Solutions of detergents were made by dissolving 5.00 g of the detergent in distilled water and diluting to make 500 cc of solution. Aliquots of these solutions were used for all tests except water content and ethanol-soluble materials. Ecolo-G did not completely dissolve in distilled water; only the soluble portion was analyzed.

Phosphate was determined by sulfuric acid digestion using persulfate followed by the molybdate-stannous chloride method of analysis for orthophosphate. Interference by silicate was noted with this method, but the error introduced by metasilicate in concentrations similar to those in detergents was equivalent to less than 0.1% phosphate. Analysis for the method of Murphy and Riley (18), which is less sensitive to silicate, gave results in agreement with the stannous chloride method for samples of Ecolo-G.

Silicate was determined by the molybdate method. Although all forms of silica may not be detected by this method of analysis, it is expected that in basic detergents all soluble silicates should be molybdate active. The insoluble silicates in Ecolo-G were ignored. Reagent grade sodium metasilicate eneahydrate was used as a standard. The weight loss of this material on drying at 110°C was 36%, which corresponds to formation of the trihydrate. Sodium metasilicate is expressed as the trihydrate, since this is the hydrate formed under the conditions of the water content measurement.

Nitrogen compounds were determined by Kjeldahl digestion, distillation, and Nesslerization of the ammonia produced. Only three detergents, Cold Water All, Lemon Low Suds No. 311, and Concern, contain more than 0.1% nitrogen.

pH was determined for 1% solutions of detergents using a Corning Expanded Scale pH meter, Model 12. The pH of solutions at the concentration recommended for top-loading washers was measured; the volume of water per washer load was assumed to be 60 l (16 gallons). Carbonate was determined by potentiometric titration with 0.2M hydrochloric acid. Since silicate does not give a distinct endpoint in this titration, a correction for silicate was made using the silicate data. The agreement between carbonate calculated from the first endpoint (pH 8.3) and the second endpoint (pH 4.6) in the titration generally agreed to within 1% sodium carbonate. In the titration of All, it was observed that a weak base with a pH of less than 3 was present. The sodium salt of NTA is a weak base which was found to give a similar titration curve.

Ethanol-soluble materials were determined gravimetrically using 2 g of detergent. The presence of brightners was determined by the fluorescence when the detergents were irradiated with ultraviolet light. Anionic detergents were determined by the methylene blue method (19) and are expressed as dodecylbenzenesulfonate. The amount of ether-insoluble anionic surfactant (eg. xylenesulfonate) was less than 0.05% in every detergent. Densities are averages of at least four determinations.

Borate was determined by potentiometric titration using mannitol.

Chloride was determined by argentometric titration using Mohr's method. Samples were ignited at red heat before analysis, since it was found that without ignition detergents gave higher apparent chloride values, and the precipitated silver chloride had appreciable spurious infrared absorbance indicating contamination of the precipitate. For ignited samples, the silver chloride did not display spuriour ir absorbance.

Water content was determined by weight loss at 110°C of 2-g samples of detergent. Samples were dried until constant weight was obtained (24 hours, except for liquid formulations). The weight loss measures volatile substances other than water, but these are expected to be minor constituents of the formulation. Under the conditions of drying, sodium carbonate is dehydrated completely, but sodium metasilicate is dehydrated only to its trihydrate.

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