

HIGHLIGHTS

Analysis of recent production of Santophen®-1 and 93% Dichlorophenol (DCP) has shown up ppb-levels of tetrachlorodibenzo-dioxins (TCDD's). These were not present in analyses carried out last year, and we believe that they can be eliminated by minor changes in plant operations. The Santophen contaminant has been identified as the relatively non-toxic 1,3,6,8-isomer; it is not considered a serious hazard at present levels.

Both Sterox® NJ and A-225 LAS look promising as aids for sand dewatering. Sulfonated H230L failed: it shows too much sensitivity to water hardness.

A low-cost, low-cleaning formula for Lysol Disinfecting Cleaner, based on Santophen, has been submitted to Lehn and Fink for their evaluation.

Our John Doe hospital cleaner formulation surprisingly failed its anti-TB activity test. We will repeat the test, at the cost of four months' time.

A new type of pump promises significant cost/energy savings for Kearny's STP manufacturing operation.

Replacing IMP with DCPD in Colgate Dental Cream apparently will require larger particle size than we now routinely make. Colgate claimed that fluoride stability required coarser material, and our results support that assertion. Carondelet operation may need to be modified.

The Montana detergent phosphate ban bill was killed, 31-14, in the State Senate. Action in Ohio will begin late in April.

NEW PRODUCTSULTRAPHOSPHATE FIBERSHuman Safety

Corporate R&D's BioMed research group proposed and has begun work on an in vitro test for fiber biodegradation. If successful, this should give us an early indication of the degradability.

The proposed test uses homogenized rat lung tissue kept in a culture medium. They will monitor appearance of phosphate as an indication of degradation.

Both this experiment and the in vivo work proposed by EHL would be facilitated by availability of radiolabelled fiber. We have located a source for labelled (³²P) H₃PO₄, and have begun discussions with MIC-Applied Sciences about getting this converted to fiber.

A/C Pipe

A visit to Certain-Teed confirmed their interest in asbestos replacements. They have staffed an R&D effort to evaluate candidates, including alkalai-resistant (AR) glass, pitch-based carbon fiber, Kevlar®, and Monsanto's material. Only AR glass has been tested so far, and it fails the autoclaving step.

We estimated manufacturing costs for AR glass fiber, and concluded that at ca. 200M lb/yr., it could be sold profitably at 60¢/lb. Thus the present \$1.50/lb. selling price reflects low volume and an attempt to recover development costs more than an intrinsic expense.

BUILDER U

Hydrocarbon Oxidation Route to Monomer

Analytical method development is complete, except for a continuing investigation of polarography by CRL.

Conditions have been defined for the conversion of glyoxylic acid to the methyl ester hemiacetal without using the expensive dimethoxypropane reagent previously required. A conversion level of 95% is obtained using a total of three times the theoretical methanol in a sequence of three stages of esterification and $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ stripping. Conversion of the resulting hemiacetal to methyl glyoxylate monomer by the P_2O_5 method gave 10% higher yield and better monomer purity than is obtained with conventional hemiacetal. We are now studying the behavior of hemiacetal from the new process in the production of monomer by thermal cracking.

Exploratory Route Bypassing Esterification

A polymeric form of sodium glyoxylate was readily made by heating solid sodium glyoxylate methyl hemiacetal (made from glyoxylic acid, methanol, and NaOH) with evolution of methanol. The resulting polymer salt has a similar XRD crystal structure to that produced earlier by heating sodium glyoxylate hydrate with evolution of water; but the reaction takes place at a lower temperature and apparently with less byproduct formation. Attempts at gas phase endcapping were not successful. We are now trying to achieve in situ solid state endcapping by incorporating low levels of acetal salts which can undergo favorable transacetalization reactions with the growing polymer ends during the polymerization step.

DEWATERING AIDS

Further studies of sand dewatering by vacuum filtration have shown that nonyl-phenol-10EO (STEROXONJ) is effective using either deionized water or water with hardness at the level expected at a Pennsylvania Glass Sand (PGS) plant. A-225 LAS also performs well at both hardness levels. However, the effectiveness of light highboiler (H-230L) sulfonate and Aerosol OT (an American Cyanamid dewatering aid) were significantly reduced by hardness ions. This hardness sensitivity eliminates H-230L sulfonate from further consideration in this specific application. Simulated drain pile dewatering results were consistent with the vacuum filtration data. Thus we have application potential in both dewatering methods used by PGS.

Our laboratory results were reviewed with PGS in March. Cost savings potential in their drying operations appears to be the most important benefit to them, although a secondary consideration in at least one of their plants is increased through-put. They have requested samples as well as toxicity and biodegradation data in order to evaluate the impact of our surfactants on other plant operations. We have agreed to evaluate a sample from their Oklahoma plant to test applicability of our dewatering aids on a different type of sand.

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A review of our vacuum filtration results was also presented to Dorr Oliver. We supplied them with samples of our best anionic (A-225 LAS) and nonionic (NJ) candidates. They will include these materials in tests they are currently conducting for PGS.

POLYPHOSPHATES FOR SAND WASHING

The use of polyphosphates to improve the efficiency of the washing operations used to clean marginal quality glass sands is under investigation in our laboratory. SHMP and TSPP, but not STP, appear to have definite deflocculation effects under our test conditions. Hopefully this will translate into better clay and ferric oxide removal from the sand surface. We are currently awaiting analytical results before planning additional effort in this area.

DCPD REPLACEMENT FOR IMP IN COLGATE DENTAL CREAM

A series of DCPD samples, including competitive samples, have been analyzed for particle size distribution. Coulter Counter size results suggest a correlation between fluoride stability and size as Colgate indicated. Thus, the competitive (Knapsack) sample supplied by Colgate indeed had a higher mass median size than our 240 Code DCPD and better fluoride stability. The coarser cyclone portions of DCPD from the various plant mills are being evaluated for F stability. The sizes of the Carondelet cyclone fractions showed fluctuations from a given mill. Augusta cyclone portions appear consistently coarser and more uniform than those of Carondelet. The above results suggest that the Carondelet milling operation may have to be improved toward coarse size and better uniformity. This approach, in addition to adjuvants, may be required to meet Colgate requirements. Extensive paste storage tests are underway to define these approaches.

A 250-pound sample of LUSTRA-PHOS® A has been blended and sent to Colgate for flavor evaluation. This LPA sample is a backup candidate, should DCPD fail to meet the Colgate target.

SANTOPHEN®1

Lehn and Fink

As requested by Lehn & Fink, we have submitted to them our recommendations on a lower cost Santophen formulation with more modest cleaning performance (comparable to their quat-based LDC-II).

Meanwhile, Lehn & Fink Research has advised us of a potential darkening problem encountered with our proposed LDC-III prototype formulation after several weeks' storage at elevated temperature. Studies aimed at overcoming this problem are underway.

"John Doe" Hospital Cleaner

Hill Top Research has informed us that our "John Doe" hospital cleaner formulation, based upon only Santophen as the antimicrobial, did not pass the AOAC Tuberculocidal Activity Confirmation Test. A joint Marketing/Research decision has been made to repeat the test, both at the customary 1:128 dilution level and at a more concentrated 1:100 level. Several modified formulations and a standard Santophen-based commercial cleaner control will also be evaluated. Other scheduled tests on the John Doe cleaner are being postponed pending the outcome of the TB tests.

COAL/OIL MIXTURES (COM)

The role of water in our COM stabilization system has been studied and found to be very important (in agreement with results from other laboratories). Without water, only moderate increases in stability are found. With the addition of 4.5% water, however, greatly increased settling stability is observed. Contrary to some emulsion literature, we have found that the order of addition of oil, water, and surfactant has no significant effect.

It appears that our stabilizers do not function by simply increasing mixture viscosity since the stabilized mixture has a viscosity comparable to that prior to addition of water and surfactant. Avoidance of significant viscosity increase is important to potential COM users.

MACHINE DISHWASH PROJECT FOR SPECIALTY CHEMICALS DIVISION

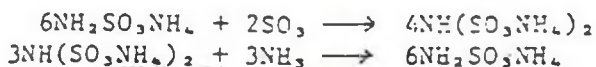
Simple replacement of Cl-TSP by AC1 and sodium sulfate, a potential cost savings approach to the formulators, resulted in a significant increase in glassware spotting to the point where it would be objectionable to the housewife. Addition of crystalline TSP to the AC1 to replace the alkalinity lost from removal of Cl-TSP reduces the spotting problem. However, this also eliminates the cost advantage from using the AC1. Further work is planned.

TSIS

A two-lb. sample of TSIS has been sent to Unilever for their evaluation as a hypochlorite bleach mitigator.

AMIDO- AND IMIDO-SULFATES

Last month we reported that a new concept to produce diammonium imidodisulfate (DAIS) from reaction of ammonia and sulfur trioxide using ammonium amido-sulfate as an intermediate was conceived. Based on raw materials, this could be the cheapest approach to produce DAIS, the precursor of trisodium imido-disulfate (TSIS). Both reactions as depicted below are demonstrated and the yields are near quantitative.



This concluded our laboratory investigation of the chemistry in producing TSIS. A final report has been prepared. Further development work will depend on market evaluations of various amido- and imidosulfates.

NEW POTENTIAL APPLICATIONS OF SODIUM INSOLUBLE METAPHOSPHATE (IMP)

Insoluble metaphosphate has a water solubility of about 0.08g per 100g water at 25°C. The dissolved IMP is in the form of long-chain polyphosphates. In our laboratory determinations, as low as 1 ppm IMP in water will inhibit the crystallization of CaSO_4 and CaCO_3 from hard water. From the rate of crystallization of calcium salts from supersaturated solutions, the dissolved IMP is at least 10 times as effective as STP in inhibition of the formation of calcium salt deposits. Since IMP is not hygroscopic, is stable in water, and dissolves slowly, it will be an ideal agent in various applications to prevent

In our first field evaluation, inhibition of scale formation in home water closet system, after three weeks, all our voluntary families gave favorable results. We plan to expand this concept to prepare IMP containing composite tablets with the capability of inhibiting bacteria and algae growth. This novel approach seems to have a vast potential.

EXISTING PRODUCT SUPPORT

ENERGY SAVING IN STP MANUFACTURE

Encouraging laboratory and pilot plant tests have been conducted on the "dry mix" type of slurry that is present in the No. 1 STP plant at Kearny. A Moyno progressive cavity pump handles this high-solids slurry with surprising ease and, at the same time, converts it to a smooth creamy slurry that is more fluid than the pump feed. A plant scale test of this pump is scheduled for early April at Kearny.

Both the synthetic soda ash now used at Kearny and natural soda ashes from California and Wyoming have been mixed with 86% H_3PO_4 and circulated in a pump loop for 20 minutes as the reaction progresses. Product slurries were then dried, milled and calcined. All STP produced had assays >91% vs. current plant product of ~88% and target of 92% minimum. For reasons not yet known, the synthetic soda ash produced higher assay (94%) STP than did the natural soda ash (91%). The cause for this difference is being investigated.

SAB

LAN Byproducts

Plasticizers Division purchases LAN (light aromatic naphtha) from our SAB process, for use as a plasticizer additive in the manufacture of floor tile. Recent shipments have contained "low boilers" which adversely affect performance. Laboratory studies have identified these undesirable components as paraffins, and recommendations will be made which should correct the problem.

Catalyst Recovery

Matthey Bishop is no longer interested in recovery of platinum from our spent platinum-on-aluminum catalyst. Negotiations are underway with Engelhard Industries to recover the platinum from spent catalyst as well as supplying us with the recovered platinum salt (platinum diammine dinitrite).

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Lever A-225

Lever Brothers is currently testing alkylate produced from the tray bypass test. This product, containing approximately 11 ppm C₃-, low boiling paraffins, will be used as a standard alkylate for perfume evaluation tests. Preliminary evaluations should be complete next month.

Raw Materials - Ethyl Olefin/Paraffin

60M lbs. of Ethyl C₁₂₋₁₄ olefin/paraffin feedstock was successfully demonstrated last month at Chocolate Bayou. An additional 250M lbs. is currently being tested, and after two weeks of operation on heavy alkylate, no significant process problems or catalyst deactivation have been observed. If no major problems are encountered for the remainder of the run, this feedstock will be approved and used at a rate of approximately 5M lbs./year in the process.

WASTE HEAT RECOVERY FROM PHOSPHORUS COMBUSTION

Mechanical completion of the Long Beach test system is scheduled for the week of April 16. The pressurized water loop for heat transfer and corrosion testing will be installed under the crossover of the No. 2 acid plant. The test section will be inserted initially in the crossover itself, with plans for subsequent relocation to the combustion chamber. Test operation is planned for the rest of this year.

SANTOPHEN-1 DISINFECTANT FORMULATIONS

Methodology for analyzing Santophen-1 in formulations, needed to support EPA registration, has been developed. It has been applied both to Monsanto's "John Doe" and several commercial products. Additional studies include method development for mixed phenolic systems and storage stability aspects. Prior to the issuance of our method to our customers, we are exchanging samples and analyses with Dr. J. B. McDevitt from LSU, who is independently developing methodology, under EPA Auspices.

TCCO REGISTRATION

The FDA announced in the March 9, 1979, Federal Register, that the Topical Anti-microbial I is being reopened. The agency will consider additional data not considered by the panel or in the Tentative Final Monograph. Of most interest to us is data submitted by P&G on the safety and effectiveness of TCC and data submitted by the SDA on the safety of antimicrobial soaps in infants. Colgate's data on the combination of TCC and DP-300 will also be considered.

As we reported previously, this may delay final action on our "Category I" status until 1982 or later.

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ENVIRONMENTAL ACTIVITIES/PHOSPHATE DEFENSEMONTANA

Our efforts to prevent passage of a ban succeeded: the Senate defeated the House-passed bill 31-14. Key to the success was credible testimony from a retired chemistry professor now a legislator, the manager of Stauffer's Silver Bow P. plant, and a local manufacturer of I&I detergents. Their words and the relative conservatism of the Montana Senate did in the proponents. Nevertheless, we expect the measure to arise again in the next session, in 1981.

OHIO

No activity yet on a recently-introduced ban bill. We expect hearings "after Easter". Procter and Gamble has taken the lead in this fight, and they believe the bill can be defeated.

NTA

EPA is still rewriting their technical assessment; last we heard, it was going thru a fourth draft. Probably no decision will be made before May.

Procter and Gamble believes that they can persuade the National Cancer Institute to say, in effect, that NTA poses little or no threat to man as a carcinogen. P&G has developed extensive evidence showing that NTA's carcinogenicity in rats results from metabolic changes at high feeding levels. This may convince NCI that it is relatively harmless. If successful, of course, this will greatly lessen P&G's risk in product reformulation. It has, however, slowed down EPA's decision-making.

HUMAN SAFETY"DIOXINS" IN CHLOROPHENOLS/SANTOPHENO-1

Analysis of three recent production lots showed that Santophen-1 contains no detectable (<10 ppb) 2,3,7,8-tetrachlorodibenzodioxin, relieving somewhat our anxieties about this product. The one sample of 93% 2,4-dichlorophenol (DCP) analyzed showed about 90 ppb of this or one of the other four indistinguishable isomers. We suspect that dioxins form during purification of DCP; we've begun work to confirm or contradict this. If it's correct, dioxin formation can be essentially eliminated.

Both Santophen and DCP contain quantities (~30 and ~300 ppb, respectively) of a contaminant tentatively identified as 1,3,6,8-tetrachloro dibenzodioxin. This material, orders of magnitude less toxic than the 2,3,7,8-isomer, forms by the self-condensation of 2,4,6-trichlorophenol, a byproduct of DCP manufacture. The condensation requires heat and strong base, conditions which are present during distillation of the product chlorophenols. (Caustic is added to the still pot

to scavenge residual HCl, and retard corrosion.) Also under these conditions, the 1,3,6,8-isomer may slowly rearrange to a mixture of thirteen isomers, including 2,3,7,8. Under the conditions used for analysis, the isomers most likely to form first could probably not be distinguished from 2,3,7,8; they would be reported as it. (One of these, 1,3,7,8, is nearly as toxic as 2,3,7,8; the others are much less so.)

If dioxins are in fact forming in the still pot during distillation, they could be greatly reduced or eliminated entirely by use of some other HCl scavenger. We are now considering alternate approaches.

Work has begun at MRC-Dayton to identify the source of dioxins in the chloro-phenol process. We expect results by May 1.

PERSONNEL

PATENTS

U.S. 4,143,125 issued March 6, 1979 to D. R. Dyroff and W. F. Suchanek, "Calculus Inhibitors; Composition and Method."

U.S. 4,144,226 issued March 13, 1979 to M. M. Crutchfield, V. D. Papanu and C. B. Warren, "Polymeric Acetal Carboxylates."

U.S. 4,146,495 issued March 27, 1979 to M. M. Crutchfield, V. D. Papanu and C. B. Warren, "Detergent Compositions Comprising Polyacetal Carboxylates."

PRESENTATIONS

M. J. Dolan presented a paper entitled "Coal/Oil Mixtures as a Fuel Alternative" at the St. Louis AIChE Section Spring Symposium on March 20, 1979.

STATISTICS

Exempt	54.0
Non-Exempt	<u>10.5</u>
Total	64.5

J. W. Cross, H. W. Kilbourne,
E. A. Matzner, G. J. McEwan, and J. D. Wilson

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HUMAN SAFETY

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