INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO Distribution List* AT DATE June 29, 1973

FROM Dr. R. T. Gottesman AT COPY TO

SUBJECT MONTHLY SUMMARY - JUNE

Attached are copies of the Monthly Summary reports for June 1973 covering the activities of the Piscataway laboratories and associated pilot plants at Piscataway, Flemington and Reading.

R. T. Gottesman

RTG/ec

Attachments

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1-184

INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO Dr. R. T. Gottesman AT Piscataway DATE June 29, 1973

FROM Dr. F. Buono AT Piscataway COPY TO

SUBJECT

MONTHLY SUMMARY - JUNE 1973

I. COATINGS INDUSTRY

A. Microbiocides

1. Biocide and Compatibility Screening (E. DiBella, P. Minieri, H. Sidi, G. Trautenberg, G. Tirpak, G. Kagan, M. Landau)

(a) TID Candidate Compounds

Lower level biocide screening was completed on the fourteen compounds (from a group of fifty-eight) which were reported last month to have significant antimicrobial activity at 2%. The candidates which continued to show excellent biocidal responses without major paint incompatibilities, plus two additional maleimide compounds synthesized and screened this month, are as follows:

(1) Tetrahydro-3,5-dimethylaminopropyl-2H,1,3,5-thiadiazine-2-thione dihydrosulfide
(2) Tetramethylol melamine
(3) Maleimide,N-(2,6-dimethyl)phenyl
(4) Maleimide(2-methyl-6-ethyl)phenyl
(5) Maleimide(2,6-diisopropyl)phenyl
(6) 1,4 Dimethylolpiperazine
(7) Maleimide(2-methyl-6-chloro)phenyl

Paint compatibility evaluations have been initiated on compounds (3), (4), (5) and (7). The remaining materials will be evaluated when additional quantities are made. Can preservative evaluations are scheduled for compounds (1), (2) and (3).

Paint stability (4 weeks at 120°F) and can preservative evaluations on the eight promising low cost formaldehyde-releasing TID compounds are underway.

Twenty-five additional TID compounds are currently undergoing primary biocide screening.

(a) TID Candidate Compounds (continued)

* Can preservative evaluations were completed on nine TID compounds. Three materials (shown below) gave biocidal responses comparable to Nuosept 77 and are scheduled for paint compatibility evaluations.

(1) 1,2-Dihydroxymethylbenzimidazole
(2) Tetrahydro-3,5-dibutyl-2(H)1,3,5-thiadiazine-2-thione
(3) Morpholine N-(4,5-dihydro-6-methylpyridaz-3-one-2-yl) methyl

* Paint compatibility evaluations have been completed on four TID fungicide candidate compounds. Morpholine, H-(methylbenzimidaz-1-yl)methyl: Ethylene glycol showed acceptable paint performance in both latex paints and has been exposed at Piscataway and Puerto Rico. O-anisaldehyde, N-methylhydrazone was unacceptable in either paint, while the remaining two, β-dimethylaminopropiophenone hydrochloride and N-hydroxymethyl-5-chlorobenzotriazole, were acceptable in PVA and exposed.

* (b) Tenneco Pasadena Laboratory Candidate Compounds

Paint compatibility studies have been completed on the four promising Pasadena candidates. All were found unacceptable in both PVA and acrylic due to excessive yellowing and/or objectionable odor.

* (c) Chevron Candidate Compounds

Results on weathered films containing NU-74-3 and NU-4-5 indicate that NU-4-5 is much superior to NU-74-3 both in terms of zone formation and surface fungal resistance. Superior zone formation, but not surface fungal resistance, is obtained with NU-4-5 when compared to both Fungitrol 11 and 22. Further studies with NU-4-5 are underway.

(d) Maybridge Chemical Company Compounds

A quarterly report on the biocide screening of forty Maybridge compounds has been issued. Two compounds showed significant activity:

(1) N-(2,6-diethyl-phenyl)maleimide
(2) 2-amino-4-methylquinoline.

The maleimide derivative provided the structural lead for four of the active compounds listed in section (a).

Twenty additional Maybridge compounds have been submitted and are undergoing primary biocide screening.

* 2. Fungitrol 11 (G. Trautenberg, G. Kagan, G. Tirpak, M. Landau)

Dispersion Studies
The dispersion formulation containing 50% Fungitrol 11 in Nuosperse 657 and mineral spirits has been selected for further studies because of the superior shelf stability (at 120°F) over dispersions containing 55% and 60% active compound. Paint prepared with the aged 50% Fungitrol 11 dispersion is currently undergoing fungicidal evaluation.

* 3. Fungitrol 22 (G. Trautenberg, G. Tirpak)

Zone of inhibition and surface fungal resistance evaluations on weathered and unweathered vinyl films showed no increased biocide efficacy when bis(trichloromethyl)sulfone (the additive in Vinyzene BP-10) or the active ingredient in Nuodex 100VT (dodecyl dimethyl benzyl ammonium naphthenate) were added as adjuvants to the Fungitrol 22 formulation. Details of these studies are in Research Report 3006-3.

Our program to screen active TID compounds as vinyl biocides is continuing. Sixteen compounds, including all of the maleimide candidates, have been selected for evaluation.

B. Driers

* 1. Loss-of-Dry Inhibitor (G. Kagan, M. Landau)

Blends of 1.2% Cobalt/2.1% Calcium/3.2% Zinc at 2% and 0.6% Cobalt/2.1% Calcium/3.2% Zinc used as loss-of-dry additives at 2% and 3% on vehicle solids still look promising after two months' aging. Corroboration of these results are underway in several paint formulations and one month data is still being gathered. The green trim test enamel which was expected to lose dry has not shown this effect after one month. Examination of this paint for loss-of-dry will continue another month.

2. Water Dispersible Driers (G. Kagan, M. Landau)

In four water thinnable coating systems (three air dry and one baked), the Cyclodex driers (Co, Pb, Zr, Ca) performed as well as Cincinnati Milacron's water-soluble products both initially and after the paints were aged one month at 120°F. The tests included viscosity, pH, gloss, hardness and dry times. Aging the driers at 120°F for two weeks prior to incorporation in paint had no adverse effect on their paint functionality with the exception of Cyclodex lead which exhibited a longer initial dry time than the room temperature sample.

* 3. Low Temperature Driers (G. Kagan, M. Landau)

The major problem of lead replacement in oil-based house paints with equivalent drying performance at low temperatures (~50°F) has not yet been resolved by the coatings industry. None of the commercially available auxiliary metals which we have examined, i.e., Ca, Zn, Zr or Ce have shown any promise as replacements for lead under these drying conditions. Recently, in a preliminary evaluation, barium was tried as a replacement for lead in two customer oil-based house paints and, although equivalent drying performance to lead was not demonstrated, barium showed some very promising results. Additional evaluations of barium are currently underway. In anticipation of toxicity restriction with barium, a preliminary extraction test of a barium-based coating has indicated less than 0.6% barium metal was extracted. This is well within the 1.0% limit currently suggested by EPA. Nevertheless, because of the potential toxicity problem with barium, driers based on the relatively "non-toxic" strontium will also be evaluated for this application.

II. LUBRICANTS

* A. New Base Fluids (M. Knapp)

Three neopentyl polyol esters were obtained from Hatco (Hatcol 3912, 3914 and 3955) for evaluation as potential base oils for high temperature lubricants. Preliminary screening for oxidation stability was done utilizing Tenneco Method FL-8 with the following results:

Oxidation Stability (24 Hours @190°C)

Fluid*		Hatcol 3955	Hatcol 3912	Hatcol 3914	DTDA
Viscosity @100°F, cSt		29.3	82.5	100.6	29.6
Viscosity Change, %		+ 3.9	+ 1.8	+ 1.7	+ 4.9
Acid Number Change		+ 0.08	+ 0.09	+ 0.11	+ 0.17
Sludge, mg/gm oil		1.21	0.02	0.03	0.33
Corrosion	Fe	Tarnish	Tarnish	Tarnish	Tarnish
	Cu	"	"	"	"
	Al	No Change	No Change	No Change	No Change
	Mg	"	"	"	"
	Ag	"	"	"	"

* All fluids compounded with a high temperature anti-oxidant package.

A. New Base Fluids (continued)

Based on these results, Hatcol 3912 and 3914 are preferred. All three fluids were also compounded into greases and subjected to 190°C in thin layers. Again, Hatcol 3912 and 3914 were found to be superior.

Optimization of the additive package is currently underway with the initial objective being development of a superior replacement for Anderol 761 High Temperature Grease.

B. Lubricant Additives (M. Knapp)

A sample of a new, reportedly outstanding extreme pressure (EP) additive identified as "ATA" (arsenous tetrathioantimoniate) was obtained from Keystone Lubricants for evaluation. This material is an insoluble fine brown powder with an LD_{50} of 7.5 grams/kilogram (practically non-toxic). It is recommended for dispersion in both oils and greases.

Initial tests at levels lower than Keystone's recommendation (5%) indicate that it is an effective EP agent at levels as low as 0.1%. High temperature oxidation studies are currently underway.

* C. Reformulation of Anderol 536/537 (M. Knapp)

A reformulation of these products was necessitated by the sudden unavailability of one of the components, Alox 575. Both 536 and 537 are rust preventives with 537 being a concentrate and 536 being a water emulsion of 537. Candidate replacements have been developed based on analytical and laboratory test results. Rust testing in the humidity cabinet at Chestertown is currently underway.

D. Competitive Product Evaluation (M. Knapp)

Ultrachem recently developed a match for Shell's Tivella A synthetic speed reducer lubricant. A sample of this material was obtained from Boston Gear Company where they are currently using it in one of their gear reducer models. Our evaluation of this product gave the following results:

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D. Competitive Product Evaluation (continued)

Competitive Lubricant Evaluations

	Ultra Chem Grease	Tivella A	Anderol 735
Product Type	Semi-fluid grease	Semi-fluid grease	Semi-fluid grease
Base Oil Composition	Polyether	Polyether	Diester
Worked Penetration	490	380	460
NLGI Classification	000	0	000
Four-Ball Wear, mm	0.6	0.6	0.4
Four-Ball Weld, kg	160	110	160

Anderol 735 is our recommended product for this application.

F. Buono

FB/amp

INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO	Dr. R. T. Gottesman	AT	Piscataway	DATE	June 29, 1973
FROM	Dr. A. J. Deinet	AT	Piscataway	COPY TO	
SUBJECT	MONTHLY SUMMARY - JUNE 1973				

I. CHEMICALS/SPECIALTIES

1. Phosphates (L. Schinasi)

* Previous procedures for the preparation of BD-307 were based on charging either all of the required epichlorohydrin or phosphorus oxychloride to the reactor followed by gradual addition of the other reactant. The presence of such large amounts of unreacted materials during the early stages of these procedures was felt to be potentially hazardous on a commercial scale. It has now been demonstrated that BD-307 of excellent yield and quality can be obtained by a procedure in which separate streams (in their correct stoichiometric ratios) of epichlorohydrin and phosphorus oxychloride are simultaneously charged to a reactor at 110-120°C. containing a "heel" of BD-307 and magnesium oxide catalyst. The reaction proceeds smoothly, requires no wash step and has shown a 93% yield of product (based on $POCl_3$). As an extension of this technique an approach utilizing a continuous overflow reactor will be evaluated.

2. p-Hydroxybenzoic Acid (M. Reale)

* Work is continuing on a process for isomerizing dipotassium salicylate to dipotassium p-hydroxybenzoate utilizing conditions compatible with the Garfield salicylic acid plant. One of the major problems has been the phase change from a powdered solid to a paste-like fluid and back to a hard non-free-flowing solid which presented agitation problems. We have now found that a slower programmed heating rate can completely eliminate the liquid phase, evidently by isomerizing sufficient material at a low temperature, so that the system does not pass through a low melting eutectic point on a final heat-up. The total isomerization time is seven hours with two hours required at the top temperature of 275°C. This initial work indicates a yield of at least 90% with excellent color. No inert solvent is required. Corrosion rate against carbon steel was found acceptable at 2.6 to 3.6 mils per year. Further confirmatory work will be carried out since this procedure would be entirely compatible with the sal acid plant. Trial runs at Bethlehem will be recommended if our initial data is confirmed by work currently in progress.

II. PLASTICS INDUSTRY

1. Flame Retardants (M. Reale, J. Stanaback, E. DiBella)

Some additional laboratory work is underway on our prime fire retardant plasticizer, diphenyl (1,3-dichloropropyl)phosphate, to resolve some minor problems which were indicated as the result of recent pilot plant runs. These include the development of suitable reaction control points and a re-programming of time/temperature rates to minimize excess entrainment losses through the condenser.

Polyurethane foam preparations with two Butler candidates, N-phenyl di(2,3-dibromopropyl)phosphamide and N,N-di(2,3-dibromopropyl phosphoryl)diaminoethane, showed self-extinguishment but some adverse physical properties such as foam shrinkage for the first material and incomplete rise and tight foam for the second. Further tests are warranted since reformulation may correct these deficiencies. Further evaluation of our poly(polychlorobenzyl)phosphonate at Hazleton has indicated some foam shrinkage due to too high a degree of polymerization. Additional material of a lower degree of polymerization is being prepared.

A higher ester (e.g., octyl) of a simple unpolymerized dialkyl-o-chlorobenzyl phosphonate is also being prepared for screening together with three other materials selected from our existing list of candidates as low volatile flame retardant PVC plasticizers for automobile use.

The screening of isophthalonitrile, various levels of manganese carbonate, and other inorganic manganese compositions indicated all of these materials to be ineffective as smoke suppressants in polyurethane foams. To-date we have found no materials suitable for this purpose including materials related to those patented for this use in rigid foams.

As the result of continued screening aimed at preparing an emulsified T-2,3-P for the textile industry we have achieved a system stable at the required 10% T-2,3-P level on dilution with water. This was achieved by diluting T-2,3-P with an equal weight of TOF to lower its density and formulating with Tergitol P-28 and NP 27 emulsifiers. This material will be sampled to the textile industry after additional work to optimize this system is completed.

A program aimed at preparing various suitable formulations and extending the use areas of Pasadena's hexabromobutene-2 has been undertaken. The poor solubility of this material precludes the formation of a true solution, but preliminary results indicate the polyvinylpyrrolidones may achieve stable dispersions in water. Hexabromobutene itself is too unstable in flexible polyurethane formulations resulting in foam collapse. The use of organic phosphites and epoxides to nullify dehydrohalogenation is being evaluated.

III. DYES AND INTERMEDIATES

A. Intermediates

* 1. Oxalyl-p-Phenylenediamine (M. Feldman)

Laboratory work has been completed on a process for the self-manufacture of oxalyl-p-phenylenediamine (OPPD). This work was undertaken since the sole domestic manufacturer (DuPont) notified us of discontinuance of this item. Our process is based on an earlier Reading plant procedure to which we have added the recycle of certain process streams as featured in a DuPont process for added yield and lower raw material consumption. In this procedure p-nitroaniline is oxalylated with oxalic acid and the resultant oxalyl-p-nitroaniline reduced with iron to OPPD. Samples of our material were converted to Direct Blue O which was found acceptable in all evaluation tests at Reading. Yield of OPPD based on p-nitroaniline is 96%.

2. Leucotetra (M. Feldman)

The current process used for the manufacture of Leucotetra at Beaufort involves a multi-step process in which anthrarufin is converted to Acid Blue 45 and this reduced to Leucotetra. The laboratory has been looking at an alternate approach which represents a shorter synthesis scheme and could represent increased productivity and lower raw material costs. In this approach we have chlorinated anthraquinone to 1,4,5,8-tetrachloroanthraquinone and are now studying its hydrolysis to the 1,4,5,8-tetrahydroxy compound which on reduction with sodium hydrosulfite yields leucotetra. Possible means of hydrolysis for the tetrachloro compound are either caustic fusion or treatment with sulfuric acid/boric acid. The current Beaufort process will also be re-evaluated by R&D since consistent yield and quality are not achieved.

3. Durofix Replacement (H. Sidi)

As a result of the favorable evaluations shown by our initial set of candidates in comparison to Durofix NYL and Chromasist 2R, additional samples have been prepared and submitted for evaluation. These samples utilized various ratios of naphthalene sulfonic acid to dihydroxydiphenyl sulfone (DDS) to formaldehyde in the condensation in order to arrive at optimized cost/performance. Commercial DDS is offered by Monsanto at 70¢/lb. and this material represents the major contributor to the cost of our product. As a possible cheaper substitute, condensation products utilizing partial as well as complete replacement of DDS by trichlorophenol were also prepared and submitted for evaluation. Attempts to completely or partially replace DDS with a cheaper phenolic such as bis-phenol A were unsuccessful due to gellation of the product. It is anticipated that evaluation of the current set of samples will lead to finalization of our product.

B. Dyes

Yellow 4GLP Liquid (L. Port, H. Gosch)

* Work has been completed on a liquid formulation for use in the paper trade. A 40% formulation in polyethyleneglycol-water has passed all paper dye tests and found to be acceptable. The formulation itself also showed acceptable stability, viscosity and odor and a Laboratory Process Proposal will be issued.

Golden Yellow RP Liquid (L. Port, H. Gosch)

* A 40% stable formulation based on a triethyleneglycol-water system has been developed for use in the paper trade. This material has passed all paper tests and shown complete acceptability in our evaluations. A Laboratory Process Proposal for its preparation will be issued.

Orange C (M. Feldman)

Orange C is one of a line of dyes produced at Reading which utilizes 1-naphthylamine, a material included in a recent government list of hazardous substances requiring special handling precautions. As an approach to circumvent special handling a modified Orange C based on substitution of 1,6-Cleve's Acid (1-aminonaphthalene-6-sulfonic acid) for 1-naphthylamine was prepared. Dye tests, however, showed this material to be an unacceptable substitute for Orange C since it yielded considerably redder shades and heavier multifiber staining on cotton, viscose and wool. Poor build-up from light to heavier shades was also indicated.

A. J. Deinet

AJD/srf

INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO Dr. R. T. Gottesman AT Piscataway DATE June 29, 1973

FROM Mr. I. Huppert AT Piscataway COPY TO

SUBJECT MONTHLY SUMMARY - CHEMICAL DEVELOPMENT
JUNE 1973

I. CHEMICALS/SPECIALTIES

A. Phosphates

* 1. Dibromopropanol (S. Cinco, H. Gould)

Work was instituted on the development of a continuous solvent process for the preparation of DBP which would not infringe on existing patents. Preliminary data indicates this to be a feasible approach. Yields of distilled DBP, in limited trials at 10-15° and 30-35°C were in the 84-86% region with purities ranging from 98.9 to 99.7% DBP. The most recent work at 35-45°C, with residence times of 3 to 4 minutes, gave an 84.6% yield of distilled DBP (assay not available yet). This short residence time is expected to permit commercialization in a small reactor. The procedure entails simultaneous addition of solvent (chlorobenzene), bromine and allyl alcohol to a stirred, jacketed reactor while a continuous take-off of crude product through a bottom stopcock is in progress. This is followed by batch distillation. Continuous distillation of this crude is presently being investigated. The possibility of using a tube-type reactor is not attractive on a laboratory scale due to poor mixing; low yields of DBP were obtained. This approach should, however, be acceptable on larger scale runs. Future investigations on the above continuous procedure will deal with solvent and concentration effects.

2. T-2,3-P (J. Sandstedt, S. Cinco)

A sample of Fords bulk stored DBP was converted to T-2,3-P in the laboratory and Pilot Plant prior to implementation of the $AlCl_3$ process at Fords. Results are:

	Yield		Bleach
	on DBP	on $POCl_3$	Required
Laboratory	86.8	88.8	No
Pilot Plant 73-53	82	84	Yes
Pilot Plant 73-54	85	87	Yes

Reasons for the yield differences are being investigated. A laboratory work-up of the Pilot Plant crude (73-53) after

it had been acid and water washed gave an 84.4% ($POCl_3$) yield. This indicated that the lower yield was due to some process variation prior to the steam strip step. Pilot Plant produced DBP via the TID "heel" process was converted to T-2,3-P in 92% $POCl_3$ and 91% DBP yield and did not require bleaching. This duplicated laboratory experience and verified that equipment and operations were satisfactory. The Fords $AlCl_3$ trial has been postponed until the yield and scale-up differences are solved at the pilot level.

Attempts are in progress to determine why the MgO catalyzed process consistently gives lower yields than the $AlCl_3$ process. A T-2,3-P (Pilot Plant 72-46) sample was treated with gaseous HCl for 5.5 hours at 90-95°C in the presence of the standard quantity of MgO catalyst resulting in a 1% w/w absorption of gas. Subsequent analysis showed substantial degradation of the starting T-2,3-P by the HCl.

	Untreated T-2,3-P (72-46)	After HCl Treatment
Dibromopropanol	0.08%	1.40%
Tribromopropane	0.07	1.82%
Unknowns	7.22	19.27%
T-2,3-P	92.78	80.73%

The same investigation will be conducted with T-2,3-P and HCl in the presence of $AlCl_3$.

Previous corrosion testing, carried out using the Celanese cellulose acetate formulation, passivated bronze and T-2,3-P from Fords Plant (Lot No. 73-42) and Michigan Chemical, showed these materials to behave in a satisfactory manner. A previous "Tenneco" T-2,3-P from the $AlCl_3$ process (Pilot Plant Lot No. 72-46) caused severe discoloration and corrosion when in contact with virgin bronze. This same, now passivated bronze, in contact with T-2,3-P made from Great Lakes DBP in the $AlCl_3$ process, showed this T-2,3-P to be equivalent to that from the Fords Plant (MgO process) and Michigan Chemical when used in the Celanese formulation. A Research Report (No. 1908-11, June 11, 1973) was issued summarizing this work.

B. Fuel Oil Additives (J. P. Sandstedt, M. Q. Ceprini, I. H. Cooper, A. Fischer)

The ammonium soap process for preparing Chromium 8-X was successfully demonstrated in the Elizabeth Plant during the week of June 13-20, 1973. A yield of 17,100 lbs. (95%) of Nuodex Chromium 8-X was obtained for delivery to United Aircraft

who are presently evaluating this additive in land-based turbine engines at power plants throughout the country. The combined sodium and potassium level was 0.002% or less (spec. 0.02% maximum). The viscosity of P+ was an improvement over the laboratory (V) and Pilot Plant (S) values.

The Pilot Plant prepared two drums (799 lbs. net) of R-406 in fulfillment of an order from Cosmopolitan Chemicals. This magnesium-iron-manganese system is a replacement for the lead-containing NUODEX D-1759.

The laboratory process for NUODEX X-1247 (10% magnesium naphthenate) was verified. Processing difficulties were overcome by increasing the excess magnesium sulfate level from the 7%, recommended by the laboratory to 10%. Material is now available for customer and licensee sampling. A Pilot Plant Process Proposal will issue in July.

* C. Benzoic Acid (M. Q. Ceprini, A. Fischer)

Hydrolysis of benzoic acid still bottoms (Benzotar), which has an approximate composition of 15% benzoic acid, 48% benzyl benzoate, 24% benzoic anhydride and 13% non-volatiles, was carried out for four hours using 5 to 10% excess equivalents of sodium. A commercially feasible process is under investigation involving fuel oil extraction of the hydrolysate after adjustment to pH 6 to remove tars, followed by toluene extraction to selectively remove the benzyl alcohol and then toluene solution of the benzoic acid after acidification of the aqueous phase. It is anticipated that the fuel oil extract can be burned, that the toluene-benzyl alcohol fraction can be recovered by distillation and that the benzoic acid extract can be fed directly into the distilling columns of the Garfield benzoic acid facility. Over 85% of the benzoic acid values present in the "Benzotar" are recovered in the toluene extract. This will be more than one million pounds per year of additional benzoic acid production. In another work-up procedure 89% of the potential benzoic acid values present were recovered as an off-white solid (99.9% GC assay). This was done by adjusting the hydrolysate to pH 5.6, decolorizing with Darco S-51 and filter aid, precipitating the benzoic acid down to pH 1 at 60°C and finally, filtering and drying.

D. Chlorination Technology

1. 2,4-Dichlorobenzoyl Chloride (J. DeGaetano)

Using a $FeCl_3$ catalyzed hydrolysis over a two hour period at 110°C, 2,4-dichlorobenzotrichloride was converted to 2,4-dichlorobenzoyl chloride in 95% yield. The product quality is well within production specifications.

	Analysis	Specifications
Assay,%	98.7	96.0, Minimum
Color, APHA	15	50, Maximum
Congealing Point,°C	20.8	16.5, Minimum

Trials with zinc chloride (64 hours) or mixed zinc chloride-magnesium oxide(24 hours) catalyst systems were unsuccessful. Addition of the water in the $FeCl_3$ process over an 8 hour period to simulate plant limitations of HCl handling, caused no difficulty. In this case, a 94% yield of "in-spec" product was obtained. Normal water addition, followed by 20 hours of reflux before distillation showed no yield or quality loss of 2,4-dichlorobenzoyl chloride. However, when only half the required water was added and the reaction held at 120°C for 20 hours before completing it, only 77% yield of product was obtained. Based on problems encountered in parachlorobenzoyl chloride produced using a ferric chloride catalyst, work is underway where addition time will be extended to 12 hours and distillation time to 6 hours.

II. PLASTICS INDUSTRY

A. Additives

1. Tin Stabilizers (E. Szabo, H. Gould, S. Hoch)

Samples of laboratory prepared IOTG were converted to NUOSTABE V-1562 and evaluated by the Flemington Applications Laboratory. The IOTG's varied in the source of"oxo" isooctyl alcohol used for esterification with thioglycolic acid. All samples were equal to the laboratory prepared control in pressed plaque clarity and color. However, only one of them was equal to the control in oven heat stability testing, namely, the one made using Ashland Chemical alcohol, without subsequent distillation for purification of IOTG. Since this represented the most economical approach, repeat preparation for verification is in progress.

Evaluation of Aceto Chemical's DBTO showed it to be equal to a laboratory control in pressed plaque clarity and color but slightly poorer in oven heat stability. Since the use of Aceto's DBTO represents a modest cost saving and since the availability of a secondary supplier is desirable, modified V-1562's (with 5% "tris") were prepared and determined to be functionally acceptable.

NUOSTABE V-1528 (Plant Lot No. 69480) containing precipitated material (due to overcharge of DBTO) was treated with 0.25 to 1.0% I-46 after filtration. Only the samples containing 0.75% and 1.0% I-46 remained stable and were evaluated along with a sample treated with IOTG (by Elizabeth Plant personnel). The sample treated with added IOTG (in a molar amount equal to the DBTO overcharge) was found to be functionally acceptable by the Plastics Applications Laboratory.

2. Stabilizer Intermediates (S. Hoch)

Matches for Ferro's FDA stabilizers containing zinc, calcium and magnesium benzoates and stannous stearate in epoxidized soybean oil were prepared. These samples were made where the respective salts were heated at 150-160°C in a.) NUOPLAZ 849, b.) a 1:1 mixture of NUOPLAZ 849 and Polyguard (FDA phosphite). Samples were also made in which the benzoates were prepared in situ in the above two solvent systems. These materials will be functionally evaluated after metals analyses are successfully completed.

Reaction of barium chloride with sodium hydroxide to yield barium hydroxide resulted in the desired formation, but due to solubility in water, losses were experienced. A summary of three runs is listed below:

Sample No.	Reactant Concentration as $Ba(OH)_2$ in Water, %	Barium Hydroxide Yield,%	Chloride,%
E-019:10A	15.3	61.0	3.3
E-019:10B	19.6	72.4	2.9
E-019:10C	24.5	70.5	11.4

Emphasis on studying this route as a replacement for commercially unavailable barium hydroxide will be continued.

A Pilot Plant Process Proposal for the manufacture of I-237 Stabilizer Intermediate, using the wet fusion method, was issued. Studies were initiated on the preparation of the material by dry fusion in the Pilot Plant's Abbe paste mixer. Results from the initial runs tabulated below demonstrate the feasibility of the technique; however, additional work is required to "zero in" on operating conditions and time cycles.

	Analysis	Results	Specifications	Remarks
D-028-148	Moisture, %	0.84	1.00, Max.	All materials
	Free Fatty Acid,%	3.00	3.00, Max.	charged at outset;
	Color	Brown	White	1% excess barium; unreacted cadmium.
D-028-149	Moisture, %	1.3	1.0, Max.	Stoichiometric meta
	Free Fatty Acid,%	2.0	3.0, Max.	charged; sequential
	Barium,%	8.1	7.7-8.1	charging order; no attempt to vacuum d:
D-028-154	Moisture, %	2.7	1.0, Max.	Stoichiometric meta
	Free Fatty Acid,%	4.6	3.0, Max.	charged sequentiall;
	Barium, %	7.9	7.7-8.1	additional water an
	Cadmium, %	14.4	14.4-15.1	acetic acid charged
	Color	Off white	White	no attempt to vacuu dry.

3. Stearates (J. Sandstedt, S. Hoch)

Dry blends of DLG-20, S-1244 and magnesium stearate (USP) and varying amounts of wetting agents were made to produce water dispersible materials. The best results, based on water dispersibility, were obtained with Aerosol OT-B at 5.0% use level. These materials are available for customer evaluation. Two samples of S-1244 (Ca stearate) were prepared, one in tap water and one in deionized water for subsequent evaluation by Amoco. After analyses are completed, the samples will be transmitted to the customer. This work was done in an attempt to determine causes of rejection of our S-1244 by Amoco.

B. Plasticizers

* 1. Alcohol Substitutes (O. Fuchs)

Functional evaluations by the Flemington Applications Laboratory of n-hexyl-isodecyl phthalate (NHIDP) in a 40:60 ratio (n-hexyl:isodecyl), indicated this material to be a promising candidate as a substitute for DOP. A total of 4-1/2 gallons of additional plasticizer has been prepared by the laboratory for further testing at Flemington (E-004-91, E-004-101). Two other NHIDP samples containing hexyl:isodecyl ratios of 50:50 and 75:25 were also prepared for similar testing. Substitutes for di-tridecyl phthalate (DTDP)(E-004-97) and di-tridecyl adipate (DTDA)(E-004-99) were prepared in the laboratory using Neodol 23 alcohol in place of tridecyl alcohol. Neodol 23 is a mixture of linear C_{12} and C_{13} alcohols produced by Shell. These esters will be sent for functional comparison to their tridecyl alcohol counterparts, both as plasticizers and lubricants.

2. Polymeric Plasticizers (R. Caruso)

A third batch of POLYESTER IX was run in Chestertown according to the revised Pilot Plant Process Proposal 1502-6 (Revision 2), modified to reduce plant time cycles below 24 hours. Both acid number and viscosity specifications were not achieved; attempts to rework the batch were unsuccessful. The material initially produced had an acid number and viscosity of 3.0 and 140 cs @ 210°F, respectively; the reworked material resulted in an acid number of 2.5 and a viscosity of 130 cs @ 210°F. Subsequent analysis and laboratory work-up of the prepolymer showed it to be comparable to Pilot Plant material.

	Plant	Pilot Plant
Hydroxyl Number	64	64
Acid Number	0.62	0.44
Viscosity cs @ 210°F	168	165

Conversion to PE-IX	Lab Conversion	Pilot Plant
Acid Number	1.7	1.96
Viscosity	174	161

Samples of the plant product were submitted to Flemington for functional evaluation. This work shows the problems to be associated with determining the correct palmitic acid charge for Chestertown operations. Variable amounts of palmitic acid are distilled from the reaction mass under vacuum.

* 3. Plasticizers (I. H. Cooper)

The Artisan falling film evaporator was installed in the Piscataway Pilot Plant. Evaluation of this unit for continuous alcohol removal from various plasticizers has begun.

III. COATINGS INDUSTRY

A. Can Preservative (R. Caruso)

The hydroxymethylation step (using a filtration technique process) was run in the Pilot Plant. Approximately 16 pounds of product was recovered in hand; 28 pounds of an expected 30 pounds, based on laboratory experience, has been accountable. Major problems were encountered during the final quenching and crystallization, in that the solids tended to agglomerate. This was possibly a result of the minimal agitation levels used.

The evaluation of the hydroxymethylation using a trituration procedure is underway. A comparison of the two techniques and a critique of the overall can preservative synthesis in its present form will be made in July so that process development work may be completed.

B. Pigment Dispersant (J. Gerrity)

Evaluation of the laboratory process for R-125 Pigment Dispersant is completed. Product meeting chemical, physical, and functional requirements has been produced. Determination of optimal filtration requirements for plant operations is required since inordinate quantities of filter aid and recirculation times were required in the Pilot Plant to achieve product brilliancy. It is planned to use a Sparkler Filter on the pilot scale to solve this problem.

IV. COLORS

A. Liquid Dyes (G. F. McClain)

1. Duronyl Fast Black KPD Liquid (Textile)

Three mixes were produced during June for a total of 11,322 pounds. A Pilot Plant Process Proposal has been written and if the plant equipment can be readied in time, the next mix should be made in the Reading Plant under the guidance of Pilot Plant personnel.

2. Sky Blue M Liquid (Paper)(G. F. McClain)

Based upon performance in the Pilot Plant a Process Proposal for this liquid was written, and succeeding manufacture should be in the Reading Plant with the initial production under indirect supervision by Pilot Plant personnel.

B. Intermediates

1. p-Aminoacetanilide (G. F. McClain, E. Reinhold)

The delays in getting ice for manufacture of PAA Ba 6 in May resulted in a yield that was only 66% of theory when 80% was expected. Early in June the ice system in the Azo area was repaired and when a good supply of ice was assured BA 7 was started. The four salient changes as set forth in the May report were utilized in producing Ba 7, the processing was done without incident and all cycles were as projected.

The yield as deliverable PAA was 78% of theory and an additional 2.7% was recovered in the wash liquors for the succeeding batch, hence the total yield is 80.8% of theory versus 80% expected. The filtrate contained only 26.8 pounds of real PAA which is 80.5% of the theoretical yield, the product loss in the filtrate was reduced from 63.8 pounds on Ba 5 to 26.8 pounds for Ba 7 and the reduction in loss was achieved by concentrating the batch by evaporation to 50% of the original volume prior to precipitation. Strength of the PAA presscake is 91.3%. Functional evaluation and analytical testing are not complete. A rough cost calculation will be made based upon the above results before proceeding with further Pilot Plant work.

2. Metanilic Acid (J. DeGaetano, L. Schinasi)

In preliminary developmental runs, nitrobenzene was sulfonated and then reduced to give metanilic acid (metaminobenzene sulfonic acid) in 72% yield (assay corrected) with an assay value of 96%. Analysis of a sodium salt solution prior to isolation indicated an 84% yield at this stage. Laboratory prepared metanilic acid was then converted to GLN base in 90% yield based on amino content. Conversion of the GLN base to Yellow G via phosgenation followed by dyeing applications testing will determine the acceptability of "in-house" prepared metanilic acid.

3. Tolidine Base Dyes (G. F. McClain, E. Reinhold)

The Plant Process Laboratory has developed a method to substitute o-tolidine for benzidine in the synthesis of the benzidine series of dyes. Some promising results were obtained on Black GX in which a dye was produced that could be "shaded" to code with a green component. Based upon those results a pilot batch was run. The performance paralleled the lab work in that the shade was somewhat red, however, the tinctorial strength was only 180%. The minimum strength that will allow for the addition

of the necessary shading components is 250%. The low strength is apparently due to a high volume which resulted in a need for large quantities of salt for complete precipitation. Four significant points have been found in the process that can be changed which will result in a reduction in volume and improvement in the tinctorial strength. The batch was split into two parts and the yield on part A is 105% of that expected, part B is not dry. Based upon the above data, a second trial batch is being scheduled.

4. Scarlet MG (For Red NAS Liquid)(G. F. McClain)

To confirm the ammonium chloride precipitation that was done on Ba 149, two drums were taken from Ba 150 and moved to the Pilot Plant. The batch was precipitated with ammonium chloride using a procedure outlined by Colors Synthesis Group. The precipitation was normal, but filtration and washing were difficult and slow. The presscake will be evaluated as soon as it is discharged from the press.

* 5. Benzidine From Hydrozobenzene (E. Reinhold, L. Schinasi)

A progress report has been issued which covers the work done in the Reading Pilot Plant lab. Hydrazobenzene is rearranged with HCl to form benzidine and the benzidine thus formed is tetrazotized in situ and coupled to an amine to form the dye. Preliminary results are encouraging, but work has been halted pending an interpretation of OSHA regulations, and TID interest in maintaining a position in benzidine based colors.

C. Dyes

1. Polysperse Yellow 3G (G. F. McClain)

The last pilot batch of Yellow 3G had a strong odor of trichlorobenzene, even after washing with isopropyl alcohol and large amounts of water. To remove final traces of TCB a sample was dissolved in the lab in water and caustic and heated to 95°C for a few minutes until no odor of TCB remained. The sample was then cooled and re-precipitated with HCl. The resultant crystal was soft, well defined and filtered well with no odor of residual TCB. The batch was then treated similarly in the Pilot Plant and presscake samples sent to Paterson for evaluation; the initial dyeings were green and dull - probably due to contamination. The samples are being redyed and when results are obtained, we will utilize this technique or some modification of it in isolating a portion of the next batch which is to be run in July.

The vertical leaf filter, on loan from Piscataway, is also being prepared for a trial filtration on Yellow 3G.

VI. MISCELLANEOUS (I. H. Cooper)

The Artisan falling film evaporator was tested by representatives of the Newport Division in their process development work for NUPEL 900 emulsion. Technical support and manpower were provided by the Pilot Plant staff.

I. Huppert

IH/sgf

INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO Dr. R. T. Gottesman AT Piscataway DATE June 28, 1973

FROM Mr. H. R. Johnson AT Piscataway COPY TO

SUBJECT MONTHLY SUMMARY - JUNE 1973
ANALYTICAL SERVICES

METHODS DEVELOPMENT (N. Conzo, I. Wakeman)

1. 2-Aminonaphthalene-5,7-disulfonic acid (ADS): Detection of Impurities by TLC - Procedure No. M-000.82

2. Triphenylphosphite: Determination of Hydrolysis Products - Procedure No. GC-74.0

MISCELLANEOUS

1. Triphenylphosphite (S-256) (I. Wakeman)

   Four different lots of S-256 from Weston (new samples, not previously opened) showed an average of 0.86% diphenyl phosphite, with a range of 0.5 to 1.13%. This confirms our opinion that commercial triphenylphosphite samples inherently contain acidic esters because of the ease with which the product hydrolyzes. Hydrolysis data on S-256, and the above analyses, are being supplied to Siegle for their use in opposing a German patent on phosphites which claims addition of acidic esters as an improvement.

2. Environmental (N. Eider)

   Environmental control data were supplied to Maremont Corp., IBM, General Tire and Rubber Co.. and Kendall Co. in reply to requests for impurity levels and potential carcinogens in Tenneco products. In view of the recent OSHA emergency temporary standard on carcinogens, we can expect a large number of inquiries pertaining to this standard. Except in the case of certain dyes, analytical work will not be required to answer the customers' requests.

H. R. Johnson

HRJ/sgf

I-184

INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO Dr. R. T. Gottesman AT Piscataway DATE June 29, 1973

FROM Mr. R. S. Miller AT Piscataway COPY TO

SUBJECT MONTHLY REPORT - JUNE 1973

PLASTICS INDUSTRY

Additives

1. Flow Modifier (D. Goodman, M. Koral, M. C. Spalding, E. Szabo)

A haze problem continues to exist with Supercryl 100 as compared to Acryloid K-120N. Utilizing a pressed thick plaque technique as a screening test and light transmission and haze data from the Flemington Applications Lab. it was determined that only a marginal improvement in haze was achieved by the substitution of Avirol POL-1-N for the regular surfactant at the Fords plant.

A direct comparison of lab dried flow modifier resin versus plant dried resin was made by sampling latex made at the beginning of the Avirol experiment which confirmed earlier observations that lab dried resin provides less haze than plant dried resin.

	% Light Transmission	% Haze	Appearance, Thick Plaque
K-120ND (Control)	97.6	3.0	Clear
Plant Latex, Plant Dried	96.0	5.5	Hazy
Plant Latex. Lab Dried	96.5	4.4	Reduced Haze

Based on the possible contribution of the plant drying process to the haze problem, an attempt was made to change spray dryer conditions during the Avirol campaign. A study of flow modifier lots that were reported to give satisfactory performance in customers' applications was made. The spray drying records of these lots (002, 017, 023, 025, 027) revealed that they were processed at a higher outlet temperature (185°F. vs. 170°F.) and lower pressure differential (1/2" vs. 1 1/2" vacuum) than current conditions. The functional testing of segments of resin dried at the following conditions gave about equivalent results.

170°F. Outlet Temp., 1 1/2" Press. Differential (Standard)
185°F. Outlet Temp., 1 1/2" Press. Differential
185°F. Outlet Temp., 1/2" Press. Differential
180°F. Outlet Temp., 1/2" Press. Differential

There were no appreciable improvements in haze.

In addition, a study of spray drier cleanliness was made by collecting wall scrapings after the Avirol run had been completed. The wall scrapings gave an unexpectedly good performance in functional tests.

	% Light Transmission	% Haze	Appearance, Thick Plaque
E-014-23-A, Plant Control	95.8	5.0	Hazy
E-014-23-E Wall Scrapings	97.3	3.9	Reduced Haze

These wall scrapings are being analyzed to determine what provided the improved results. We speculate increased surfactant in the scrapings.

There is also the possibility that combustion gases from the indirect-fired burners are leaking into the drying chamber. Process Engineering will explore this as well as other spray dryer conditions in order to optimize product quality.

In the laboratory the influence of incremental addition of monomer to provide a more uniform comonomer sequence is under study. In respective runs, ethyl acrylate and methyl methacrylate were withheld and added to the reaction incrementally. The pressed plaque screening test showed improvement with ethyl acrylate added incrementally. These results were confirmed by the Applications Lab. A slight worsening with added methyl methacrylate was noticed, although this result needs to be confirmed.

Methanol extraction of Acryloid K-120N showed 0.65% ash (as $Na\ SO_4$) vs. 0.2% in Supercryl. Sodium lauryl sulfate was identified as the surfactant extracted from Acryloid K-120N with superior haze free properties.

2. Impact Modifier (J. C. Fisher, D. Goodman, M. Koral, M. K. Rosen)

The Pilot Plant has scaled up the initial laboratory 3 stage graft polymerization process to the 300 gallon stainless steel E reactor and developed methods for monomer addition and proper agitation. This vessel provided a significant quantity of latex which was used to develop engineering data on the various isolation and drying processes being considered for a plant process.

The graft impact modifier polymerization was found more succeptable to wall scaling and required a higher level of agitation in the 300 gallon reactor than the Supercryl 100H process which was run in this same reactor. Acceptable, mechanically stable latex was achieved on the third batch.

Coagulation studies with Pilot Plant latex which is then dewatered on the Fletcher basket centrifuge indicates that the centrifuge cake will contain 30-50% moisture depending on the coagulation technique employed. Most promising is the use of Mg Cl_2/H Cl which produces the 30% moisture level and was verified on the laboratory and 200 gallon scale. Vacuum filtration was less reproducible and troublesome compared to centrifugation as a dewatering method. The Pilot Plant Mikro-Pulverizer was found unsatisfactory for breaking the centrifuge cake prior to feeding the Strong Scott dryer. A low shear cake breaking device seems more desirable.

Direct spray drying of latex at Nichols Engineering and drying of centrifuge wet cake in the Pilot Plant Strong Scott dryer have both shown the impact modifier product to be quite heat sensitive and difficult to dry to the < 0.5% moisture content required.

A summary of the drying conditions studied is shown below:

Dryer	Inlet Temp. °F	Outlet Temp. °F	Volatiles %
Nichols Spray Dryer	285	135	10.2
Nichols Spray Dryer	305	150	3.1
Nichols Spray Dryer	405	200	0.7
Strong Scott	200	130	2.0
Strong Scott	200	145	3.0
Strong Scott	250	160	1.2-2.0
Strong Scott	225	175	0.6-0.8

The Nichols dryer showed considerable tendency toward wall build-up at temperatures above 300°F. Nichols personnel indicate that this can be overcome by proper dryer design and they indicate that a dryer could be designed to operate economically at a 150°F. ΔT for this process. The existing Fords Supercryl dryer only appears good for 400 lb./hr. based on trials to date. Another one day trial at Nichols has been scheduled by Process Engineering to finalize the feasibility and economics of spray drying.

Drying tests in the Strong Scott appear more promising and better performance is expected now that the coagulation and centrifuge steps have been improved. This work is continuing.

Freeze coagulation of latex followed by centrifugation produces a 10% moisture content wet cake and a very dense desirable dried product. Sandvik is determining the feasibility of using their continuous belt freezer to coagulate latex.

PVC Resins

1. Pasadena PVC Process (D. Goodman, J. C. Fisher, F. Kantzler, M. Koral, D. Kryzwicki, M. K. Rosen, N. Eider)

A number of requests for flow sheet review, pollution analysis and design data have been answered in the following areas.

a. Raw Material Analysis
b. Physical Properties of Raw Materials and Process Solutions
c. Physical Properties of Resins for Bulk Handling Equipment
d. Effluent Water Composition and Treatment
e. Molecular Sieve or Activated Carbon Treatment of Air Emissions

2. Chemical Foam Blending Resins (J. C. Fisher, M. K. Rosen)

Burlington BR-501 continues to be acceptable in the foam wicking test although performance has diminished. BR-501 slurry was obtained from Burlington, treated with sodium bisulfite and its performance is being evaluated to determine if best wicking performance can be restored without interfering with other resin properties. If successful a plant trial with sodium bisulfite will be requested.

R. S. Miller

RSM/srf