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

TO Distribution List* AT DATE March 30, 1973

FROM Dr. R. T. Gottesman AT Piscataway COPY TO

SUBJECT MONTHLY SUMMARY
MARCH 1973

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

R. T. Gottesman

RTG/ec

Attachments

Distribution List*

Mr. M. Freifeld
Dr. D. Keyworth
Dr. P. A. Lobo
Dr. T. E. Maggio
Dr. M. Rosen (2)
Mr. G. I. Rozand
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Mr. M. Wilkenfield — File
Mr. T. T. Zuhl

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

TO Dr. R. T. Gottesman AT Piscataway DATE March 27, 1973

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

SUBJECT MONTHLY SUMMARY - MARCH 1973
ANALYTICAL SERVICES

METHODS DEVELOPMENT

1. Microbiocides (I. Wakeman, D. Tylicke)

   In connection with EPA requirements (potential effects on the environment), procedures were developed for determining the extent of leaching and volatilization of NUOSEPT 77 from paint films, and also its mobility in a typical loam soil.

   Leaching from paint films is of a low order; five 10-minute dippings in water over a 2 month period removed 1.96% of the microbicide present. NUOSEPT 77 shows no detectable volatilization from a freshly painted surface.

   By using thin layer plates prepared from loam soil (EPA recommendation), we were able to demonstrate that NUOSEPT 77 will not migrate from its point of application in the soil.

2. T-2,3-P (P. Ketterer)

   The determination of volatiles in T-2,3-P by gas chromatography has been revised to include an internal standard and to simplify the on-column injection technique (Procedure GC-51.0). This procedure is applicable to final products and in-process samples after neutralization washes.

3. Parachlorobenzaldehyde (N. Eider, P. Manzo)

   A procedure for plant control laboratory use has been developed for monitoring the sulfuric acid level during the hydrolysis of the nitrile impurity in parachlorobenzaldehyde (Procedure No. M-000.80).

H. R. Johnson

HRJ/sf

INTER OFFICE MEMO TENNECO CHEMICALS, INC.

TO Dr. R. T. Gottesman AT Piscataway DATE March 30, 1973

FROM Mr. R. S. Miller AT Piscataway COPY TO Dr. M. Rosen

SUBJECT MONTHLY REPORT
POLYMERIZATION R&D SECTION
MARCH 1973

PLASTICS INDUSTRY

Additives

1. Flow Modifier (D. Goodman, L. Gross)

The Alcolac sodium lauryl sulfate was received at the Fords plant, sampled and confirmatory laboratory polymerization runs made in the laboratory. Supercryl 100H plant trials were initiated March 30 with R&D assistance.

2. Impact Modifier (D. Goodman, L. Gross)

Evaluation of two, 12 liter impact modifier batches using SR-6189 and SR-6196 (ca. 800Å) was completed. A study of three milling times (4, 7, 10 minutes) and three impact modifier levels (5, 10, 15 phr.) showed the laboratory modifiers to be comparable to Kureha BTA-III in impact strength, modifier efficiency, color development and clarity over the range of variables studied.

Table I lists the values obtained at 15 phr. modifier at 7 minutes milling time which are the standard PVC screening test conditions.

TABLE I

Impact Modifier Evaluation

Modifier	Izod Impact (ft. lbs.)	Light Transmission (%)	Crease Whitening
D021-36 46/37/17-But/Sty/MMA SR-6189	8.09	83.0	Comparable
D021-38 46/37/17-But/Sty/MMA SR-6196	8.31	81.4	Comparable
Kureha BTA-III	7.92	81.3	Comparable

Table II shows the impact strength response to different milling time and modifier levels for the three modifiers.

TABLE II

Impact Strength at Variable Loadings and Milling Times

Modifier	Pts./100 Pts. Resin	Izod (Ft. Lbs.) Milling Time 4 Min.	7 Min.	10 Min.
D021-36	5	0.80	0.78	0.79
D021-38	5	0.72	0.83	0.82
BTA-III	5	0.78	0.80	0.82
D021-36	10	1.28	1.29	1.34
D021-38	10	1.30	1.34	1.25
BTA-III	10	1.30	1.25	1.32
D021-36	15	8.1	8.1	8.0
D021-38	15	9.2	8.3	8.5
BTA-III	15	8.3	7.9	7.5

All light transmission values fall between 81-84%.

Pilot Plant scale-up of the laboratory process has been initiated.

PVC Resins

1. Chemical Foam Blending Resin (J. C. Fisher, M. K. Rosen)

Homogenization of gelatin suspension system batches prior to polymerization yielded resins with somewhat finer primary particles but a larger percentage of agglomerates. The resins, after screening, showed poorer wicking characteristics in the foam test than non-homogenized gelatin resins. The homogenization approach has been dropped.

A one month study is in progress to verify the potential of the following approaches which have recently given improved wicking characteristics:

a. The post polymerization addition of sodium bisulfite to blending resin slurry obtained from the Burlington Plant.

b. The use of trichloroethylene (TCE) combined with lower polymerization temperature to prepare BR-501.

2. Fast Catalyst Studies Copolymer Resins (J. C. Fisher, M. K. Rosen)

EHP/LP (di-2-ethylhexyl peroxydicarbonate/lauroyl peroxide) catalyst systems were investigated to determine if productivity improvements could be gained over the standard LP catalyst system. Favorable polymerization kinetics were obtained with the 389 resin system and initial results with 314 copolymer appear promising as indicated in Table III.

TABLE III

EHP/LP Catalyst Studies - Copolymers

Resin Type	LP (phm)	EHP (phm)	Reaction Time (hrs.)	Minimum Cooling H_2O Temp. (°F)	Reaction Temp. (°F)
T-389	0.12	-----	9.3	132	151
T-389	0.12	0.005	8.0	133	151
T-389	0.12	0.015	7.3	133	151
T-389	0.12	0.025	6.6	133	151
T-314	0.141	-----	8.3	146	158
T-314	0.141	.015	6.8	140	158

A kinetic study of 315 copolymer will follow the completion of the 314 copolymer series. Functional performance of the EHP/LP catalyzed copolymer resins must be verified before these systems can be recommended for plant trials.

3. Vinyl Chloride/2-Acrylamide-2-Methylpropanesulfonic Acid (AMPS) Copolymers (D. Goodman, L. Gross)

Copolymers of 90/10 vinyl chloride/AMPS were run with eight common PVC suspending agents in a methanol/water medium. No incorporation of AMPS was observed by elemental analysis. The AMPS is only slightly lipophilic. The solubility differences even with methanol present to act as a coupling agent gave unsatisfactory large particle size suspensions. The intended products were to be post reacted with stabilizing ions to provide internal stabilization.

Coatings Industry

1. Pigment Dispersant for Latex Paint (D. Goodman, M. Koral, G. Kagan, M. Landau)

Process improvement work was reinitiated on the R-125 pigment dispersant process to reduce the level of methyl isobutyl ketone (MIBK) solvent used in the polymerization of this 1-hexene/maleic anhydride copolymer and determine whether the solvent can be recycled and purified by methods consistent with the capabilities of the Garfield Special Products Plant. In a series of laboratory polymerizations it was demonstrated that:

a. Excess 1-hexene monomer could be reduced to negligible levels.

b. MIBK could be reduced by 50% leading to a 68.6% solids content polymerization system which reduced foam problems and drastically improved batch productivity.

c. 70% of the MIBK solvent can be purified by batch distillation and be recycled to yield analytically acceptable product.

The net effect of these improvements over the original process is a 32.5% increase in productivity/batch, a 50% reduction in MIBK requirements and demonstration that 70% of the MIBK is recyclable by simple techniques compared to the original plan of scrapping this stream.

Functional testing has yet to be completed on all the laboratory samples. Assuming that the products are functionally acceptable additional confirmatory runs will be made and a Laboratory Process Proposal will be issued.

Table IV shows details on the laboratory runs.

TABLE IV

Pigment Dispersant Resins

Notebook C200-176 Run No.	Maleic Anhydride (Moles)	1-Hexene (Moles)	Polymer Content, Effective Solids (%)	Recycle	Comments	Coatings Lab Evaluation
1	2.0	2.10	51.8	None	5% xs 1-Hexene	Satisfactory
2	2.0	2.02	52.3	None	1% xs 1-Hexene	Satisfactory
3	2.0	2.02	57.8	None	20% less MIBK	Satisfactory
4	2.0	2.02	62.6	None	35% less MIBK	Pending
5	2.0	2.02	68.6	None	50% less MIBK	Pending
6	2.0	2.02	68.6	Distilled MIBK		Pending
7	2.0	2.02	68.6	Dried MIBK	Polymerization Inhibited	
8	2.0	2.02	68.6	Dried and Distilled MIBK		Pending

2. Kromosperse (D. Goodman, L. Gross, G. Kagan, M. Landau)

With Pentek in short supply an evaluation was completed to determine whether Monopentek could be substituted for Pentek in the preparation of Nuodex I-160 for Kromosperse manufacture. The charge of Monopentek was adjusted to achieve the same relative hydroxyl content as Pentek and presented no problems. The Kromosperse sample with Monopentek was found functionally equivalent to the Pentek Kromosperse control in Coatings Laboratory tests.

R. S. Miller

RSM/srf

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

TO Dr. R. T. Gottesman AT Piscataway DATE March 30, 1973

FROM Dr. F. Buono AT Piscataway COPY TO

SUBJECT

MONTHLY SUMMARY - MARCH 1973

I. COATINGS INDUSTRY

A. Microbiocides (P. Minieri, H. Sidi, E. DiBella, G. Trautenberg, G. Tirpak, G. M. Kagan, M. Landau)

1. Screening (Biocide and Compatibility)

(a) TID Candidate Compounds

Further studies (lower level testing) on the six previously reported promising biocides still demonstrated unacceptable paint compatibility. Interestingly, isonicotinic acid azide, which showed excellent broad spectrum biocidal activity, demonstrated variable paint compatibility in successive evaluations indicating instability of the compound. The Synthesis group will attempt to develop stable derivatives.

Twenty-six TID candidates were primary (biocide) screened (2% and lower levels where warranted) this month. One compound, tetrahydro-3,5-dibutyl-2(H)-1,3,5-thiadiazine-2-thione, has shown good biocidal activity and is scheduled for can preservative evaluation. Another material, morpholine, N-(2-methyl benzimidaz-1-yl) showed both bactericidal and fungicidal activity and is undergoing can preservative and paint compatibility evaluations.

An additional twenty TID candidates have been submitted and are undergoing screening.

(b) Maybridge Chemical Candidate Compounds

A summary report on the screening of 50 Maybridge compounds has been issued. Four compounds showed significant antimicrobial activity but some incompatibility. These were materials containing the -thia-1,3-diazine-6-thione moiety, and will serve as structural leads for the Synthesis Laboratory.

(c) Chevron Candidate Compound

Chevron Nu-74-3 is being evaluated in acrylic and PVA test paints at the biologically active concentrations of 1.0%, 0.5%, 0.25%, and 0.10%. At 1.0% and 0.5%, the pH of both the acrylic and PVA paints dropped to an unacceptable level. At levels of 0.25% and 0.10%, the Chevron candidate showed acceptable initial performance in both paints.

In an alkyd house paint, Chevron NU-74-3, at 2% and 0.5% showed acceptable initial performance. Aging studies are in progress.

(d) Fungitrol-22

Studies to provide further information on F-22 vs. Ventron's Vinyzene BP-5 and the potential replacement, BP-10, have been completed and a research report issued. Briefly, BP-5 outperforms F-22 at equivalent treatment costs. Superior weathering properties are demonstrated with F-22, but only at higher treatment costs. However, Ventron's BP-10 proved to be superior to both BP-5 and F-22. Since the marketing price of BP-10 is the same as BP-5 and the performance of BP-10 is superior, a competitive position for F-22 does not exist.

B. Driers (G. M. Kagan, M. Landau, A. Fischer)

1. NuXtra Zirconium 24%

A second low viscosity 24% Zirconium preparation that more closely approximates the viscosity of Ferro's 24% Zirconium is being evaluated for dry time performance. Initial dry time results given in the table below show that this 24% Zirconium preparation is also comparable to the competitive product in a white enamel. Similar data is shown for the regular production NuXtra Zirconium 18% vs. Ferro's Zirconium 18% for comparison.

Initial Thru-Dry Times Hours:Minutes			
24% Zirconium		18% Zirconium	
NuXtra	Ferro	NuXtra	Ferro
2:55	3:05	2:35	2:20

2. Loss-of-Dry Inhibitor

Work on the program to develop a non-staining loss-of-dry inhibitor has now been concentrated on the use of the promising cobalt/calcium/zinc blends as non-staining loss-of-dry inhibitor additives to paints having conventional drier systems. Nuact, our lead-based loss-of-dry inhibitor, as well as Cobalt 254 are being used as comparators for these studies.

3. Cerium Driers

Several reports from Marketing have indicated that Cerium is a more effective replacement for lead than zirconium in alkyd paints. To investigate this, Cerium Naphthenate 6% was evaluated in a white enamel vs. a competitive product, Cerium Hexchem 6% (Mooney). Conventional lead and zirconium drier systems were used as comparators. Drying times of the four systems were monitored at room temperature and at 50°F (Cerium was reported to show better low temperature performance than zirconium). Since Cerium is known to stain, color measurements were also taken on the paint films. Results tabulated below show that TID Cerium Naphthenate dries slightly slower than the Mooney product at room temperature and both Ceriums show slightly faster drying than zirconium. However, at 50°F, Cerium shows essentially the same performance vs. zirconium and none of these approach the dry-time of lead under the same drying conditions. Also, both Cerium products stain (discolor) the paints considerably more than either zirconium or lead.

	Thru-Dry Times Hours:Minutes			
	Cerium Driers		Comparators	
	TID	Mooney	Zirconium	Lead
At Room Temperature	2:55	2:10	3:30	2:15
At 50°F	8:45	10:20	10:30	5:25
	Whiteness (Reflectance)			
	95.9	95.8	96.2	96.1
	Yellowness Index			
	4.7	4.7	3.1	3.1

4. Antiskinning Agents - Guaiacol Special C (G. M. Kagan, M. Landau, E. P. DiBella)

Because of limited availability of guaiacol, a program was undertaken to develop a reformulated Guaiacol Special C substituting ortho-substituted phenols for a portion of guaiacol (currently present as 40% of Guaiacol Special C).

Of six modifications of Guaiacol Special C (40/60 mixture of guaiacol/o-cresol), a composition of 20% guaiacol, 60% o-cresol, and 20% 2-isopropyl-phenol gave slightly higher (but acceptable) drying times and slightly shorter (but acceptable) skinning times, when compared to the present product at levels of 0.1% and 0.2% on paint. The data is tabulated below:

Dry Time and Skinning Characteristics
of Experimental Guaiacol Formulation in White Enamel PCL-609A

Concentration % by Weight on Paint		Guaiacol Special C 40% Guaiacol 60% o-Cresol	Experimental Composition 20% Guaiacol 60% o-Cresol 20% 2 Isopropylphenol
0.1%	Dry Times - Hours:Minutes	0:45 4:30 5:25	0:45 4:45 6:00
	Skinning Time	10 Days	6 Days
0.2%	Dry Times - Hours:Minutes	0:45 6:55 8:25	0:45 7:25 9:05
	Skinning Time	19 Days	18 Days

A laboratory process proposal for the revised formulation was issued and estimated manufacturing cost calculations indicated a cost of 54.2¢/lb. as compared to the standard plant formulation of 91.2¢/lb. Much of this is due to the lower cost of 2-isopropylphenol as compared to guaiacol.

Additional modifications with higher levels of 2-isopropylphenol are currently being tested.

II. LUBRICANTS

A. Evaluation of Octachlorobutene and Hexachlorobutadiene (M. H. Knapp)

Samples of these two liquids were received from the Pasadena Laboratory for evaluation as extreme pressure additives. They were tested for load-carrying ability and oxidation stability in a diester base oil (DTDA) using two currently used EP additives as controls (one sulfur-phosphorus and one sulfur only). The octochlorobutene was found to be somewhat effective as an EP agent, but the hexachlorobutadiene was found to be ineffective. Neither showed any advantage over the controls in this test or in an anti-wear test. Both were also inferior in oxidation stability.

Load-Carrying Evaluation

Compound	Four-Ball Wear Scar Dia., mm	Four-Ball EP Weld Point, kg	Falex EP Failure Load, lbs.
Bis(tridecyl) adipate	0.85	100	1150
Bis(tridecyl) adipate + 1% OCB[1]	0.83	140	>2750
Bis(tridecyl) adipate + 1% HCB[2]	0.88	100	1050
Bis(tridecyl) adipate + 1% DMT[3]	0.68	180	>2750
Bis(tridecyl) adipate + 1% ZDP[4]	0.43	120	1250

[1] Octachlorobutene
[2] Hexachlorobutadiene
[3] Alkyl derivative of 2,5-dimercapto-1,3,4 thiadiazole
[4] Zinc dialkyldithiophosphate

Oxidation/Corrosion Stability

Compound	Hours to Failure at 190°C
Anderol 495	>200
Anderol 495 + 1% OCB	< 24
Anderol 495 + 1% HCB	24-48
Anderol 495 + 1% DMT	72-96
Anderol 495 + 1% ZDP	< 24

B. Evaluation of Competitive Products (M. H. Knapp)

1. Mobil Jet Oil II

This neopentyl polyol ester based lubricant was evaluated to determine if it could be competitive to ANDEROL 495 compressor oil. It was found to be, surprisingly, somewhat inferior in oxidation stability as measured by our FL-8 Oxidation Test (24 hours @190°C). It did, however, offer a slight advantage in load-carrying. It might be expected that this oil would offer very nearly equal, but not superior, performance in rotary air compressors. The exact chemical identity of the base fluid is being determined.

Property	Mobil Jet II	ANDEROL 495
Viscosity @210°F, cSt	5.2	5.4
Viscosity @100°F, cSt	28.1 (133 SUS)	29.6 (140 SUS)
Viscosity Index	125	130
Pour Point, °F	-65	-70
Flash Point, °F	490	490
Evaporation, 22 Hours @210°F, %	0.5	0.8
Demulsibility @130°F, ASTM D1401, Minutes to Separation	10	5
Oxidation/Corrosion, 24 Hours @190°C, Tenneco Method FL-8,		
Viscosity Change, %	+8.2	+1.4
Acid Number Change	+0.03	+0.08
Sludge, mg/gm Oil	0.46	0.01
Effect on:		
Copper, Steel	Slight Tarnish	Slight Tarnish
Magnesium, Aluminum, Silver	No Change	No Change
Four-Ball Wear, 40 kg, mm	0.5	0.8
Four-Ball EP, Weld Load, kg	90	90
Falex EP, Failure Load, lbs.	1400	1100

2. Ore-Lube OLIMO Synthetic Motor Oil

This new automotive crankcase oil, reportedly a "synthetic," was analyzed and found to be an SAE 30 petroleum-based oil to which 0.08% molybdenum disulfide was added. Laboratory evaluations of physical properties and load-carrying performance show this product to have no advantages over ANDEROL 472, or a typical petroleum-based oil such as Havoline 10W-40.

2. Ore-Lube OLLMO Synthetic Motor Oil (continued)

Property	OLLMO	Texaco Havoline	ANDEROL 472
Appearance	Opaque, grey	Clear, Dark Amber	Clear, Dark Amber
SAE Viscosity Number	30	10W-40	10W-40
Viscosity @210°F, cSt	12.3	16.4	15.2
@100°F, cSt	123.3	94.7	93.0
@0°F, cSt	>20,000	3850	3700
Viscosity Index	98	198	182
Pour Point, °F	-15	-35	-50
Flash Point, °F	430	420	450
Four-Ball Wear, 40 kg, 1200 rpm, 167°F, 1 Hour, mm	0.4	0.4	0.4
Four-Ball EP, Weld Load, kg	170	190	200
Falex EP, Failure Load, Lbs.	1100	1125	1600

C. Evaluation of I-1121 as Replacement for EP Lead 30 (M. H. Knapp)

I-1121, an extreme pressure additive used in various ANDEROL greases, was evaluated as a potential replacement for Nuodex EP Lead 30 in two petroleum base stocks. It was found to be considerably less effective than either lead naphthenate alone or a commonly used blend of lead naphthenate and sulfur. I-1121 also was evaluated in combination with the lead-sulfur additives, and it showed an inhibiting effect.

Compound	Four-Ball EP Weld Point, kg
Dentax 90, 100%	110
Dentax 90 + 0.5% I-1121 (a)	150
Dentax 90 + 6% EP Lead 30 (b)	160
Dentax 90 + 1.2% Dibutyldisulfide (b)	200
Dentax 90 + 6% EP Lead 30, 1.2% DBDS	710
Dentax 90 + 0.5% I-1121, 6% EP Lead 30, 1.2% DBDS	180

(a) Optimum level.
(b) Commonly used levels in commercial products.

MONTHLY SUMMARY - MARCH 1973 March 30, 1973

D. Plastics "Compatible" Base Oils (M. H. Knapp, R. Stanabach)

Evaluation of two Synthesis Laboratory submissions (ditridecyl dodecenylsuccinate and methylpropyleneglycol bis(dodecenyl-succinate) indicated that both have very little effect on polystyrene, either stressed or unstressed. Their utility, however, is limited by their high viscosities. Additional DDSA esters of lower viscosity (bis(isooctyl), bis(isodecyl), etc.) are being prepared by the Synthesis Laboratory.

Eight additional compounds have been submitted by Synthesis for plastics "compatibility" testing.

F. Buono

FB/amp

I-184 (50M)

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

TO Dr. R. T. Gottesman AT Piscataway DATE March 30, 1973

FROM Mr. I. Huppert AT Piscataway COPY TO

SUBJECT MONTHLY SUMMARY - CHEMICAL DEVELOPMENT
MARCH 1973

I. CHEMICALS/SPECIALTIES

A. Chlorination

1. p-Chlorobenzaldehyde (J. DeGaetano)

The first 5,000 pound order for American Cyanamid was filled. Inadvertent dilution of the hydrolysis acid resulted in product containing less than 0.2% nitrile compared to none detectable in the laboratory preparation and ca. 2.5% in previous shipments. This run also brought to light yield problems currently being encountered in the Sommelet reaction at Fords. R & D and Manufacturing personnel are involved in a joint effort to resolve this problem.

B. Phosphates (R. Caruso, S. Cinco. H. Gould)

A rework procedure for an emulsified plant batch of T-2,3-P (Lot 72-56) has been developed where 62.5% by weight of the emulsion layer is obtained as product. The T-2,3-P so obtained however must be blended off since APHA colors of 250 and 320 were obtained after bleaching. Verification of this procedure on plant scale will be undertaken during the week of March 26, 1973. Laboratory work on an impure DBP sample (containing 91.5% DBP by GC) showed that charging $POCl_3$ on an assay basis results in significant yield improvement viz

Weight of DBP Charged	Mole Ratio DBP/$POCl_3$ Corrected	Corrected	% on $POCl_3$	% on DBP Mass	% on DBP Assay
668.4 gm	3.07	2.81	82.0	80.1	87.6
730.4 gm	3.35	3.07	93.5	83.7	91.4

The major impurity in the above work was 1,2,3-tribomopropane. A Pilot Plant Process Proposal for the manufacture of 2,3-dibromopropanol was issued. Preparation of DBP at 42°C using the "heel" process was carried out and is compared to other laboratory results below.

Reaction Temp., °C	DBP Yield %	T-2,3-P Yield % $POCl_3$	T-2,3-P Yield % DBP
10 ± 3	82.5-84	92.5-95	90.5-93
20 ± 2	82.5-84	93-94	91-92
35 ± 3	81-83.5	92-93	90-91
42	82-83.5	89.4	87.4
50 ± 2	82-83	87-90	85-88

This work shows reaction temperatures above 35°C should be avoided. FMC allyl alcohol was shown to be a satisfactory raw material (84% yield of DBP converting to T-2,3-P in 91.6% on DBP and 93.7% on $POCl_3$ via $AlCl_3$). Use of distilled DBP as reaction solvent instead of the crude DBP reaction mixture (heel) at 22°C showed no advantage. A DBP yield of 83.9% and conversions to T-2,3-P of 93.4% ($POCl_3$) or 91.2% (DBP) (equal to 20°C results in the above table) were obtained.

Corrosion testing on T-2,3-P at 60°C for eight weeks indicates that stainless steels 304 and 316 are not corroded by T-2,3-P LV grade. Lithcote LC-C-24, carbon steel, brass, and copper were slightly corroded in the presence of T-2,3-P LV. However, the T-2,3-P control at the 60°C temperature showed evidence of degradation (acid number rise, haze formation) as well as all samples in contact with the test coupons.

Work on the preparation of diphenyl dichloropropyl phosphate for customer evaluation was started in the Pilot Plant.

C. Fuel Oil Additives

1. Chromium 8-X (M. Ceprini, R. Caruso, I. Cooper, A. Fischer)

The Pilot Plant verified the revised laboratory process for preparing Chromium 8-X by the double decomposition reaction of ammonium soaps of 2-ethylhexanoic and n-hexanoic acids with chromic chloride. Yields of 96.1% were obtained in the Pilot Plant compared to 97.8% in the laboratory, differences being due to handling losses. Laboratory and Pilot Plant process proposals were issued.

A 100 pound sample of Pilot Plant prepared material was shipped to United Aircraft for functional evaluation.

2. Other (A. Fischer)

A stable fuel oil additive combination of 50% NuXtra Manganese 9%, 25% NuXtra Iron 9% and 25% Nuodex 767 (6% magnesium naphthenate) was developed for Cosmopolitan Chemical Co. Stability of the combination

was achieved by the addition of 10% 2-ethylhexanoic acid to the mixture. The recent availability of NuXtra Manganese and Iron at the 10% metal concentration permitted the accommodation of the extra acid in the combination.

D. Miscellaneous

1. Steel Belted Tire Adhesion Promoters (M. Ceprini, S. Hoch)

Analysis of Goodrich's steel belt shows the belt area to contain cobalt. Michelin's rubber to metal bonding promoter was found to contain 17.6% cobalt, Versatic 911 fatty acids and a small amount of boron. Recommendations have been made by R & D to Marketing specifying "packages" of our standard and experimental metal formulations of cobalt, molybdenum, chromium, zirconium, zinc and magnesium, to be sent to Goodyear, Firestone, Uniroyal and General Tire Companies.

II. PLASTICS INDUSTRY

A. Additives

1. Tin Stabilizers (M. Ceprini, S. Hoch, H. Gould)

BD-603, which was developed in May 1968, was shown to be a chemical and functional match for M & T's DM-8504. Chemical analyses consisting of infrared spectroscopy, differential thermal analysis, tin and solid contents, trace metal analysis as well as general degradation studies have shown DM-8504 to be dibutyltin bis-isooctylmaleate. Functional evaluation by the Flemington Applications Group showed it to be equivalent to M & T's DM-8504 in Nixon-Baldwin's applicable PVC formulation. A one pint sample of BD-603 was transmitted to Nixon for evaluation. A laboratory Process Proposal for BD-603 will be issued early in April. The precipitated solid, from BD-602 which appeared after standing one month in drums in Elizabeth, was generally identified as a dibutyltin-carboxylate-alkoxide type compound. The analogous laboratory preparation using the same raw material stocks has still not precipitated (six months). Processing and minor formulation modifications have been completed and sheet stability studies, at 0, 40 and 120°F, on the resulting compositions are underway.

A shipment of isooctylthioglycolate (IOTG) from UCB was received by Elizabeth. A sample of this material was converted to V-1562, V-1562+5% butyltin tris-isooctylthioglycolate ("tris"), V-1528's from V-1562 and V-1562 + 5% "tris", V-1902 (formerly BD-600) and V-1903 (formerly BD-601). Functional evaluation of these stabilizers by the Flemington Applications Group showed all of them to be acceptable

for commercial production except the standard V-1562. The preceding work showed that addition of "tris" to V-1528 improved its functionality over standard V-1528. This work was extended in the laboratory where a maximum functional improvement was obtained with a "tris" content of 7.6% of the total composition.

Preliminary work on the self-manufacture of IOTG has produced two preparations in yields of 87-89% (distilled) made from Ashland and USS isooctyl alcohol. Future efforts will be directed toward increasing yield, improving processing conditions and examining other commercially available alcohols (e.g. Houdry) and thioglycolic acid such as that from Gallard-Schlesinger (Germany).

2. Low Toxicity Stabilizers (S. Hoch, M. Ceprini)

Two zinc-alkanolamine complexes prepared according to U. S. 3,652,619, were found to be functionally superior to standard powdered zinc stearate PVC stabilizers by the Flemington Applications Group. Economic and commercial feasibility of such products is presently being determined. Additional preparations of calcium benzoate with low free alkalinity, using different raw materials, showed that the dry fusion process can go essentially to completion. Zinc benzoate was prepared by dry fusion at 60°C. Ca and Zn benzoates may be useful as new powder stabilizer intermediate replacements for Ca and Zn stearates. Five additional low toxicity stabilizer candidates similar to previous submissions but higher in tris compound have been submitted to Flemington for functional evaluation

3. Stearates (S. Hoch)

A plant run of DLG-20 using zinc sulfate solution containing less than 10 ppm manganese verified laboratory results by producing a storage-stable product. Four more surfactants, (Brij 35, Brij 96, Brij 56 and Renex 35) have been screened in an attempt to improve DLG-20 extrudability. No improvement in extrusion properties was observed.

B. Polymeric Plasticizers (J. Sandstedt, O. Blum, R. Caruso, M. Koral)

1. The Pilot Plant process for the manufacture of NUOPLAZ 6189 was modified, through the use of a partial condenser and a revised time-temperature profile. A reduction of 43 percent in the overall time cycle was achieved from 37 hours to 21 hours. Potential glycol economies, resulting from reduction in glycol charge requirements, cannot be obtained. Processing economies are possible, however, since the glycol content in the water of esterification was reduced from 45 to 9 percent.

The bulk of the glycol excess is recovered as organic distillate suitable for burning, thus reducing overall waste disposal costs.

2. Foam Activators (S. Hoch)

A pre-shipment sample of the Pilot Plant preparation of AG-398B was accepted at GAF and a one drum CTO shipped. A revised Laboratory Process Proposal for I-230 has been issued.

3. Monomer (J. DeGaetano)

A tentative laboratory process was developed in the laboratory in which trimethylol propane trimethacrylate (TMP-TMA) was obtained in 91.4% yield. An estimated manufacturing cost based on this process showed the project to have poor economic justification. A final process will not be developed until there is an improvement in the economic picture.

III. COATINGS INDUSTRY

A. Driers

1. Water Dispersible Driers (Cyclodex)(J. DeGaetano)

Laboratory Process Proposals for Cyclodex Zirconium 12%, Revised Cyclodex Calcium 4% and Cyclodex Calcium 6% have been issued. Efforts are continuing to develop higher metal-content Cyclodex driers with emphasis on cobalt, manganese and lead. Cyclodex driers of iron and cerium will also be prepared. Standard materials presently available are Cyclodex Cobalt 6%, Manganese 6% and Lead 24%.

2. NuXtra Zirconium 18% (A. Fischer)

A process improvement was effected in the manufacture of NuXtra Zirconium 18% whereby the water phase, amounting to about 25% of the batch weight, was mechanically rather than thermally eliminated. The separation and subsequent elimination of the water phase was achieved by conducting the reaction with less solvent (enough to yield 20% instead of 18% metal), thereby increasing the specific gravity of the product layer and causing a sharper, more rapid and complete phase separation. It was also found essential to keep the reaction temperature below 65°C (150°F) to prevent the water phase from permanently redispersing in the reaction mixture. The efforts of the process improvement are to permit an 11% increase in batch size and to eliminate about four kettle hours of drying time for a combined savings of about $25-30,000 annually. This process modification was implemented in the Elizabeth Plant immediately upon completion of laboratory work. A Laboratory Process Proposal covering the modification will be issued in April. Sodium zirconyl silicate,

a low cost zirconium source, was evaluated and found to be unsuitable for use in the manufacture of zirconium driers either by direct reaction with 2-ethylhexoic acid or by prior conversion to sodium zirconyl sulfate.

IV. COLORS

A. Intermediates

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

Continued work in the Reading Pilot Plant lab has resulted in a process in which the acid to acetanilide ratio is increased from 3.0:1 to 3.5:1; this allows for a more readily controllable nitration since crystallization in the flask is eliminated and better heat transfer is achieved. Secondly the nitration product after drowning is neutralized with 50% caustic soda solution prior to filtration, thus eliminating lengthy washing cycles in the press and the need for reslurry. Neutralization does not result in a cost increase since the acid filtrate would require neutralization at Beaufort before being allowed to go to the plant waste stream. The third revision to the Research Laboratory Procedure involves the use of a more finely ground iron (80 mesh or finer versus 60 mesh) and a slightly higher water dilution during reduction. The finer iron provides better control of the soluble iron "reducing" conditions and the higher dilution prevents the product from precipitating during the clarification step. Overall yield as p-aminoacetanilide from acetanilide is 78% of theory assayed value of the PAA. The Research Laboratory Process is 80% of theory assay value of PAA.

PAA produced in the Pilot Plant Lab when converted to Scarlet 4BNS results in a dye that is a trace bluer in shade and possessing staining characteristics "close" to code, yield is 5-10% higher than standard (the quality is good and the yield is good). A pilot batch is scheduled for the week of March 25, 1973 to check out the above findings.

2. Polysperse Yellow 3G Crude (G. F. McClain, L. Schinasi)

Laboratory work was completed and a laboratory process proposal issued. One batch was run in the Reading Pilot Plant converting Pilot Plant produced QCA. The condensation reaction was vigorous, which was expected and the isolation was quick and straightforward using the Nutsch. The presscake yield based upon solids content was 71.9 pounds versus an expected 68 pounds and the initial dyeings at Reading indicate that the shade is "close" and the staining characteristics are "close", showing that purification is not required. The tinctorial strength of the dry crude is 340% which is lower than expected. A laboratory treatment to remove solvent raised the strength to 379%, but a recrystallization only resulted in 346% strength. The solvent recovery procedure is being checked in the Piscataway Laboratory before an attempt will be made in the Pilot Plant.

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

The single mix produced in March is the only mix produced for the year and totalled 3,971 pounds. Poundage production to date which embraces three years totals 37,922 pounds. This liquid is made directly from presscake produced in the Reading Plant and the conversion is routine.

C. Thickener Press Trials and Pump Evaluations (G. F. McClain)

1. GLN Base (First Thickening Trial)

Four hundred pounds of ready to filter slurry at 31% initial solids was washed with 200 pounds of 25% salt solution in four hours. The slurry was then thickened to 45.9% solids in eight hours pumping time. Slurry assay at the start was 7.36% real and after thickening was 26.78% real.

The starting crystal size of 80-90 micron length and 8-10 micron width was reduced to 15-25 microns x 2-3 microns, plus some assorted fines. This product should readily thicken to a 45-50% slurry which could be stored in a tank until needed and then used "in situ" without a filtration step. The product "tars" on drum drying.

2. Orange 4G (First Thickening Trial)

460 pounds of ready to filter slurry at 26.9% solids was thickened to 325 pounds volume and then washed with 300 pounds of 25% salt solution in 4-5 hours. The product was then thickened to 33.6% solids in about 4-5 additional hours. The crystal was reduced from 30-40 microns at the start to 3-5 microns in the final product. The product was satisfactorily drum dried in the laboratory and could be drum dried in the plant if poundage output should warrant. The shade of the drum dried product was "close" but strength only 106% which indicates need for more wash or a wash of lower concentration.

3. Yellow G

Crystal attrition was checked on this product using first a centrifugal pump and secondly a Moyno pump. Yellow G appears to be a very durable crystal - the starting crystal of 30 micron length was only reduced to 25 micron and the reduction was the same for both pumps. The product was finally thickened using a Moyno pump and there was no further crystal breakdown. The thickened slurry was drum dried to flakes and fines and even though no #11 was used there was very little dust. The drum dried product had a spectro strength of 129% compared to a normal plant production value of 130-160%.

I. Huppert

IH/sf

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

TO	Dr. R. T. Gottesman	AT	Piscataway	DATE	March 30, 1973
FROM	Dr. A. J. Deinet	AT	Piscataway	COPY TO	
SUBJECT	MONTHLY SUMMARY - MARCH 1973				

I. PLASTICS INDUSTRY

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

Dry and moist thermal stability tests have been carried out on the two candidates which appeared promising at the Foam and Plastics Division, namely, R-293 which is phenyl bis(2,3-dibromopropyl)phosphate and R-295 its phenoxyethyl analog. Moist stability tests (pH profile in water) showed Fyrol-2 to be best and our R-293 to be equal to T-2,3-P as follows:

	pH Profile			
Time, Hrs.	FR-2	T-2,3-P	R-293	R-295
0	7.3	6.8	6.6	4.6
3	5.7	4.5	4.3	3.3
5	5.1	3.9	3.9	3.1

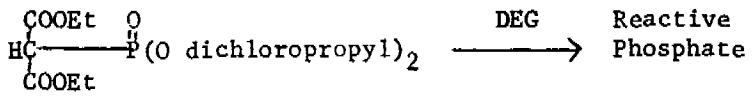
TGA determinations were run as a measure of dry thermal stability and indicated R-293 and T-2,3-P to be superior to Fyrol 2 with R-295 being the poorest. Both of our candidates are scheduled for Pilot Plant runs to provide sufficient material for more extensive evaluation. A diethyl poly(polychlorobenzyl)phosphonate was synthesized from benzyl chloride and imparted self-extinguishment to a standard flexible polyurethane foam. A pint sample was submitted to Foam and Plastics for their evaluation.

Attempts to provide T-2,3-P emulsions which are stable on dilution with water (for use on fibers) have failed, although representative samples of all commercial emulsifier types were screened. Our current approach is aimed at synthesizing a flame retardant phosphate having a hydrophilic branch e.g. a bis(2,3-dibromopropyl)phosphate derived from propane sultone such as:

$$(BrCH_2BrCHCH_2O)_2 - \overset{O}{\overset{\|}{P}} - O - CH_2CH_2CH_2 - SO_3Na$$

A 70% T-2,3-P emulsion (using polyvinyl alcohol) was sampled to Seydel-Wooley since they were interested in any formulation that exhibited even short term stability.

Other synthetic work included the preparation of a phosphate from diethyl malonate which will be condensed with diethylene glycol to provide a reactive type flame retardant candidate:



A titanium (III) salt of dichloro-α-hydroxy benzyl phosphonic acid was prepared and will be evaluated as a combination smoke suppressant-flame retardant.

II. COATINGS INDUSTRY

1. Can Preservative (H. Sidi, E. P. DiBella, R. Stanaback, O. Fuchs, P. Ketterer, J. Standstedt, I. Cooper)

Extensive laboratory work has continued on the final hydroxymethylation step aimed at a commercial process. The major remaining problem is to achieve a non-volatiles content of 5% or less (as measured by GLC) by a simple economical procedure. Although the use of substantial quantities of carbon (Darco KB) readily yields a quality product the costs are excessive. The screening of cheaper carbons has indicated Nuchar C-115N to show promise. The use of a granular carbon column as well as solvent saturated carbon are being evaluated as more efficient approaches.

Two runs were carried out in the Piscataway Pilot Plant this month to verify the laboratory process for converting o-toluidine to crude dichloroindazole. A strong evolution of nitrogen which occurred when excess free nitrous acid was removed by treatment with urea resulted in some physical losses in the first run, but this was readily corrected in the subsequent run. The yield of dichloroindazole (assay corrected) based on o-toluidine was 65% as compared to 70% obtained in the laboratory. A GLC comparison of the major peaks and non-volatiles showed the following:

Indazole	1st PP Run	2nd PP Run	Lab. Run
7 - Cl	5.88	5.52	9.98
5,7 - Di Cl	58.17	58.70	61.90
4,5,6 - Tri Cl	5.25	5.86	5.03
Other - Tri Cl	4.22	5.88	4.87
Non-volatiles	25.78	22.93	17.72

The Pilot Plant runs also indicated that sufficient presence of acid must be maintained during hydrolysis of the chlorinated aceto-toluidide to assure complete hydrolysis, and that crystallization of this material can be avoided by initiating diazotization at a slightly higher temperature.

These initial results on scale-up were very encouraging and will be followed by additional runs. The crude dichloroindazole will be held pending completion of laboratory work on the final hydroxymethylation step.

The EPA registration petition was completed and submitted for our can preservative (Nuosept 77). This petition covered data on biological efficacy, paint compatibility, toxicity, physical properties and environmental data, manufacturing procedure, product data bulletin and proposed labeling.

III. DYES AND INTERMEDIATES

A. Intermediates

1. Leucotetra (M. Feldman)

The sample of leucotetra prepared in the laboratory by a revised isolation technique and submitted to Toms River Chemical Corporation was found satisfactory in their evaluation. Laboratory work was completed and a Laboratory Process Proposal was issued on a procedure for incorporating the improved isolation technique directly into the Beaufort process. The revised technique consists of the use of a small quantity of sodium hydrosulfite prior to acidification of the final product reslurry to assure complete reduction. A TLC test was also developed as a highly sensitive means of determining completion of hydrosulfite reduction as well as final product quality.

2. Isatin (L. Schinasi)

Because of limited availability of hydroxylamine acid sulfate a sample of Commercial Solvents hydroxylamine sulfate was evaluated as an alternate raw material for the preparation of the intermediate isonitrosoacetanilide. The material was found to be satisfactory and gave normal quality and yield when converted to isatin. With hydroxylamine sulfate 0.6 mole is required per mole of aniline as compared to 1.2 moles when utilizing hydroxylamine acid sulfate. Addition of sulfuric acid for proper pH adjustment is also necessary. The availability of 2000 pounds per month of the hydroxylamine sulfate is equivalent to 1700 pounds of isatin.

3. Product Data Sheet (A. J. Deinet)

A product data sheet was prepared for Metanilic Base (GLN Base) in cooperation with Beaufort. This is a material which Mr. J. Goldman feels he can readily sell.

4. Durofix Replacement (H. Sidi)

Our efforts are aimed at developing a superior replacement for our Durofix and one which is equal to or superior to Chromasist as a dye resisting agent. Analytical evaluations showed Chromasist to contain a dinaphthylmethane sulfonate (e.g. Nycol type) and dihydroxydiphenyl sulfone. Simple blends of these materials in an aqueous system failed, however, to provide proper resist action on dyeing of mixed fibers.

As a follow-up two alternate preparations have been made and submitted to Reading for evaluation which represent condensation products with formaldehyde of various mixtures of dihydroxydiphenyl sulfone and naphthalene monosulfonic acid.

B. Dyes

1. Bond Blue BP Liquid (M. Feldman, L. Port)

A prior formulation of this material which has been in use for a number of years consisted of a fine dispersion based on the use of tripropylene glycol and water. On prolonged storage some settling occurs. Recent laboratory work has shown that the use of isopropanolamine yields a true solution which should overcome the previous solubility problems. Formulations with this amine as well as diglycolamine are being developed to provide material for paper dye evaluations.

2. Red NAS Liquid (M. Feldman, L. Port)

Extensive evaluations (paper dyes) of our liquid formulations based on the use of various amines is continuing at Reading. In addition we have also developed formulations based on the use of isopropanolamine and submitted them for comparative dye tests. Since these formulations are based on the ammonium salt of Scarlet MG an objectionable free ammonia odor is present. This has been overcome by the use of odor masking agents such as Mask 7267 or Mask 7283 (S. Schoenmann Co.) which have been judged to be acceptable.

3. Direct Blue 3RLP Liquid (L. Port, M. Feldman, G. McClain, E. Reinhold)

Previous experimental liquid formulations based on the ammonium salt of Blue D although showing acceptable dyeing characteristics on paper gave slight precipitation on storage. A new formulation based on the use of isopropanolamine (which shows excellent solubilizing characteristics) was developed and based on encouraging preliminary dyeing tests additional material was submitted for extensive evaluation. Stability tests are also underway. Freeze-thaw stability was found to be excellent.

Pilot Plant filtration studies have shown that filtration temperatures greatly effect the solubility characteristics of plant Blue D and hence ability to formulate as a liquid. A 70°C. filtration product was found more soluble than the standard plant filtrations at 85-90°C. To verify this a split plant run has carried out filtrations at both temperatures. Results are now being evaluated.

4. Orange 4GLP Liquid (L. Port)

A liquid formulation based on plant Orange 4G powder and polyethylene glycol/water was developed and found to be technically acceptable in preliminary paper dye tests. A formulation based on plant presscake will be undertaken as soon as such material becomes available to complete the development of this product.

A. J. Deinet

AJD/srf