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BFG TECHNICAL DOCUMENT

The BFGoodrich Company
Research and Development Division

Corporate Research

Quarterly Technical Summary

Fourth Quarter 1980

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CORPORATE RESEARCH
QUARTERLY TECHNICAL SUMMARY
FOURTH QUARTER 1980

Through November Corporate Research expenditures were $2,771,585 which is 94.7% of the 11 month goal of $2,925,549.

MATERIALS RESEARCH

Direct Vinyl Chloride Monomer: (Project 4003B-80) R. T. Carroll -- The object of this program is a new vinyl chloride monomer process with reduced capital, conversion, and utilities costs. Replacement of all or part of EDC cracking by direct processes can lead to such savings. Preliminary cost estimates by A. T. Schooley indicate savings may be sufficient to tolerate rather large recycle under favorable conditions and possibly minor sacrifice in yield.

Our efforts to date concentrated on non-catalytic chlorination of ethylene employing low conversion and recycle to attain high selectivity. Ethylene and HCl in the 1:2 ratio typical of oxychlorination feed was the recycle in the original concept. The assumption that HCl would serve as an inert diluent in the chlorination of ethylene proved false. It led to about 10% by-products, principally methyl chloroform and vinylidene chloride. This concept might have been attractive to BFG since these by-products sell at about twice the price of vinyl chloride. However, the required investment in additional columns to make necessary separations cancelled savings in investment. (A. Schooley)

This led us to examine the reaction of chlorine with ethylene without any dilution by HCl. We completed experimental designs to map the effect of temperature, chlorine concentration, and dilution by inert gas. Optimum selectivity for vinyl chloride requires a temperature in excess of 400°C. The combined selectivity of VCl + EDC is little influenced by temperature. Both VCl and the sum of VCl + EDC are inversely related to chlorine/ethylene ratio which limits conversion of ethylene to 20-30%. However, combined VCl + EDC selectivity of about 95% (with about 90% VCl) were obtained. Simulated recycle of EDC produced 95% VCl based on converted ethylene + EDC.

Much of our efforts during the early part of this quarter were in cooperation with Chemical Group technical personnel. We provided atmospheric pressure data for computer simulation and economic analysis of various process configurations. (A. Schooley and T. Kenat) We also worked in cooperation with John Lenczyk whose assignment was to investigate the effect of pressure. After early differences were resolved, he was able to confirm my results of about 95% VCl selectivity with simulated EDC recycle at atmospheric pressure. Increased pressure gave poor results due, I feel at least in part, to limitations associated with the 2-inch SS reactor he used.

Our work to examine the chemistry and define possible potential of ethylene chlorination directly to VCl is nearly complete. In most of our work we used sand as the fluidized reaction medium. This appears to have been a good choice, but questions remained about surface and/or catalytic effects. We have recently completed a short series of experiments in which the reactor was an open tube with minimal surface. There appears to be no advantages associated with this homogeneous system. Selectivity to VCl and EDC were lower than in fluidized sand. We are still concerned about some anomolous results which appear to be due to altered surface or catalysts. Generally a temperature of greater than 400°C is

required to produce VCl as the principal product. But we have observed instances of high VCl selectivity at as low as 350°C. Since lower temperatures might permit higher selectivity, this merits some further investigation and is planned.

Novel Low Combustibility Plastics: (Project 4008F-80) M. P. Dreyfuss -- Our objective is to study the products and chemistry of the addition chlorination of unsaturated polymers. The materials are to be evaluated for their apparently unique combustibility characteristics and for other key properties.

We have prepared a series of addition chlorinated polybutadienes in which the extent of reaction was varied systematically from about 60% to 100%. This corresponds to chlorine contents of 44% to 56.7%. The partially chlorinated samples were found to be very sensitive to crosslinking under ambient conditions. The use of an antioxidant (CAO-1) during produce isolation was necessary and led to adequately protected products. The primary incentive for preparing this series was to establish the correlation between extent of reaction and smoke/char values. Equally important, however, is the relationship between chlorine content and infrared spectrum, iodine number, T_g, density and thermal stability. This series should also give us useful insight into the conditions needed to obtain complete chlorination and the best analytical methods to use for following the reaction. The smoke/char tests are currently being carried out by Bill Kroenke. Density has proved to offer considerable promise as a quick determination of chlorine level. The densities of our samples correlated linearly with percent chlorine over the above range. We are currently obtaining additional data points using older samples on our shelf as well as preparing other samples as needed. The density of a fully addition chlorinated polybutadiene appears to be about 1.456. This compares to a value of 1.406 determined for PVC. The feasibility of developing an infrared method for determining chlorine level in these polymers is currently being evaluated by the analytical group. Iodine numbers are also being determined in order to assess the validity of this procedure for these chlorinated materials.

Since the desirable properties of chlorinated polybutadiene appear to improve with chlorine content, it is of interest to determine if and how these properties change as chlorine content is raised above 56.7%. To do this, of course, requires post substitution chlorination. We are attempting to prepare these polymers by continuing to chlorinate a completed chlorine addition reaction, but now under illumination. In this way we hope to be able to achieve a reasonably random homogeneous post chlorination. Such materials are expected to be more useful at this stage of our study than would a series of surface chlorinated powder particles. Our results to date have not been notably successful. In agreement with literature reports, it is rather difficult to chlorinate beyond 56.7% in methylene chloride solvent. Thus we are studying the use of chloroform and mixed methylene chloride/chloroform solvents. This work will receive increased attention during the next quarter.

We only carried out a few experiments in the area of interactive chlorination this past quarter. Addition chlorinations of polybutadiene were made in the presence of Butyl Carbitol (2-(2-butoxyethoxy)ethanol) and of ε-caprolactone. Both materials appeared to be quite reactive and considerable amounts were incorporated into the products. The T_g's were 47° and 44° respectively. The chlorine content of the product made in the presence of the lactone indicated

that about 30% of the double bonds contain a lactone moiety, assuming no oligomerization of the lactone. Both polymers displayed limited solubility, but pressed films were prepared without difficulty. We hope to be able to devote more time to the study of interactive chlorination in the coming year.

A research report covering our findings on and our current understanding of the addition chlorination of 1,4-polybutadiene was written this quarter.

G. S. Huvard -- Solutions of CB221 are best chlorinated by using the heat of reaction to ramp the reaction temperature to reflux conditions. Concentrations as high as 2 wt.% CB221 in CH_2Cl_2 have been chlorinated successfully. We find that injection of CH_2Cl_2 liquid into the Cl_2 gas feed rather than bubble tower saturation of the feed Cl_2 works best to prevent gel formation.

We have noted a rather strange viscosity behavior during chlorinations in the lab. As chlorine addition proceeds, the viscosity of the solution increases to a maximum and then drops abruptly at about the endpoint of the chlorination. As yet, we cannot explain this behavior - we don't even have a good hypothesis! Yet the phenomenon is very reproducible and doesn't seem to have an adverse effect on the final polymer. The final cement is about 2.3 x the original wt.% concentration so a 2 wt.% original CB solution results in a very clear, 4.6 wt.% cement that has good flow properties (not overly viscous and should be pumpable).

This reaction is being scaled to a 30-gallon reactor system. We plan sampling of the reactions for intermediate chlorine level polymers. Modifications of the reactor to be used are in progress.

We also chlorinated an SBR polymer for Bob Beauregard. Bob plans to test this material as a "coupling agent" for CPVC and impart modifiers (such as Kraton) which have poor compatibility with CPVC. The SBR was particularly easy to chlorinate. We encountered no gel problem at the 2 wt.% level (could likely go much higher) and obtained a very non-viscous product cement. This reaction will be run at the 30-gallon level should Bob find good results in his tests and request more material.

W. J. Kroenke -- We are trying to quantify the influence of chlorine concentration on smoke reduction and char formation. The samples were made by Dreyfuss under very similar experimental conditions.

We verified that the two post (substitution)-chlorinated H-H PVCs prepared by Schlegel (~65% Cl) have superior flammability characteristics. When 5 phr of MoO_3 was added to each of these low smoke polymers, the smoke in the Smoke-Char Test was completely eliminated. The addition of the MoO_3 did not change the very high char yield of >70% of the theoretical value.

We need to find out how little post-chlorination is required to give superior flammability characteristics - with and without a smoke retarder additive. We also need to find out if lightly post-chlorinated H-H PVC has better flammability characteristics than the intermediate chlorine (post-chlorinated) PVC resins studied by Dickens.

Guayule Rubber: (Project 4013C-80) E. C. Gregg, Jr. -- A report on high-yielding guayule issued.

In an expedition to Southwest Texas for wild guayule we noted considerable desert-plant growth as a result of recent rains. All the guayule had recovered remarkably from a severe drought of high temperature and lack of rain for 12 months. Both extensive flowering and seed-setting occurred on all the native guayule. Surprisingly, the guayule seedlings also survived the drought very well.

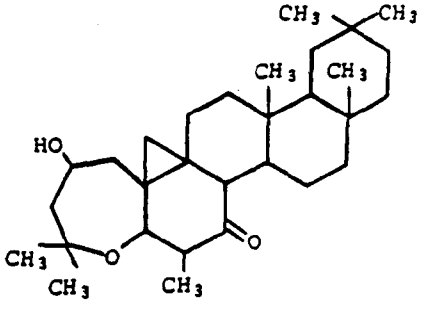
Conversation with ranch managers local to the wild guayule revealed that Goodyear has harvested about 3000 pounds of wild guayule, presumably for operation of their pilot plant for extraction of rubber from guayule. The pilot plant is in Akron. Subsequently, a photograph of uprooted wild guayule appeared in an article about Goodyear's guayule activity in the New York Times, 4 November 1980. The photograph depicted a laboratory at Goodyear Research.

We collected guayule samples from the wild and from an experimental plot of three-year-old cultivated guayule at the Texas A&M Experiment Station at Pecos. This collection of cultivated guayule was the systematic collection we alluded to earlier as a prospect. This collection is in response to the observed wide variation in rubber content from an earlier sampling of this cultivated guayule. Analysis of the rubber content of the wild guayule uncovered two bushes with 18.2% rubber. Analysis of the cultivated guayule showed one bush with 15% rubber. This bush is three years old from seeding.

Only one guayule bush with 20-weight-percent rubber was transplanted from the wild. Severe rains nearly isolated us which cut short our work. Subsequently, the arroyos filled with water and prevented our return to obtain the remaining two bushes with 20-weight-percent-rubber.

A guayule transplanter under development by the Bud Antle Co. in operation at Tempe, AZ planted 16,000 guayule seedlings per hour automatically. This is half of its capacity. Doubling the full capacity would be fairly easy and would match the field area covered by other crop machinery. The prospective commercial model could automatically transplant over 500,000 guayule seedlings per day, i.e. 40 acres per day.

^{13}C-NMR and PMR examinations of a solid compound, $C_{30}H_{48}O_3$, from guayule resin showed nearly 60 carbon atoms and more than 48 protons in disagreement with mass spectral data. This indicates that two compounds, $C_{30}H_{48}O_3$, were present. They were isolated by gpc arranged for maximum resolution. In solution their molecular sizes were different by ca. 1/30 of a carbon atom. One of this pair of compounds has the following structural assignment:



This is a derivative of a new parent ring hydrocarbon. We have named the ring parent, guayulane. The chemical name is 9,25-Cyclo,A-homo,7-keto,4a-oxaguayulan-2-ol.

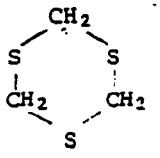
A second solid compound, $C_{30}H_{48}O_4$, similarly shows two isomers. These isomers have been isolated and resubmitted for spectral examination.

Crystalline Polymers as Engineering Thermoplastics: (Project 4015D-80) S. E. Horne, Jr. -- In the last quarterly report, I reported that phase transfer catalysis could be used to effect condensation reactions. I have been exploring the scope of this reaction to sulphide polymers.

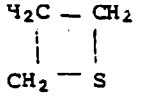
$$x(CH_2)_nX + Na_2S \rightarrow +(CH_2)_n S+_y \quad \text{or}$$

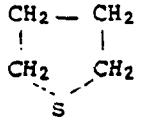

(ring compound)

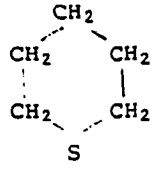
At 50°C, using aqueous Na_2S and either Carbowax 350 or benzyltriethylammonium chloride as catalyst, the following results were obtained:

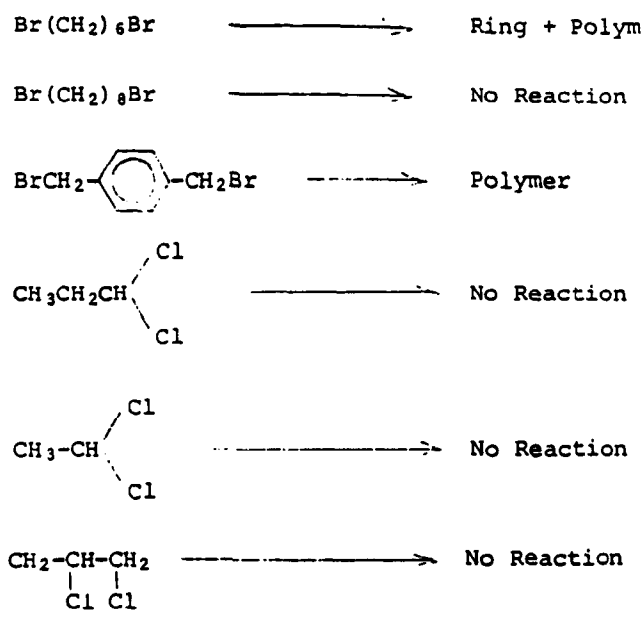
CH_2X_2 (X=Cl, Br, or I) ⟶  ring, crystalline

$ClCH_2CH_2Cl$ ⟶ $+CH_2-CH_2-S+_n$ polymer, plastic

$ClCH_2CH_2CH_2Cl$ ⟶  ring

$BrCH_2CH_2CH_2CH_2Br$ ⟶  ring

$Br(CH_2)_5Br$ ⟶  ring



I should note that the liquid ring compounds are very foul smelling. The reaction is, however, an excellent method for preparing these compounds.

There does seem to be a temperature effect. Below ~ 40°C, no reaction occurs with $ClCH_2CH_2Cl$, and at 70°C the reaction is very rapid. Holding the reaction mixture at 70° overnight produces a very foul smelling mixture so there are secondary reactions to be considered. Perhaps the dihalides that showed no reaction at 50°C will show a reaction at a higher temperature - this will be investigated.

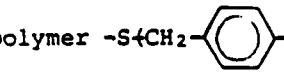
Copolymers can also be prepared from mixtures of CH_2Cl_2 and $ClCH_2CH_2Cl$. These show a gradual change from the crystalline trimer to a gummy product back to the plastic polymer from $ClCH_2CH_2Cl$.

Polymer characterization is made difficult by the insolubility of the polymers in all ordinary solvents. I am limited to characterizations that can be made on the solid materials.

DSC results on a $-S\{CH_2-CH_2-S\}_x$ polymer, 4015D-80-156B, shows some interesting results:

First heat; 0°C → 85°C, no transitions
Second heat; 0° start, Big endotherm @ 120°C another at 160°C
Third heat; 0°, endotherm @ 105°C, big endo at 160°C

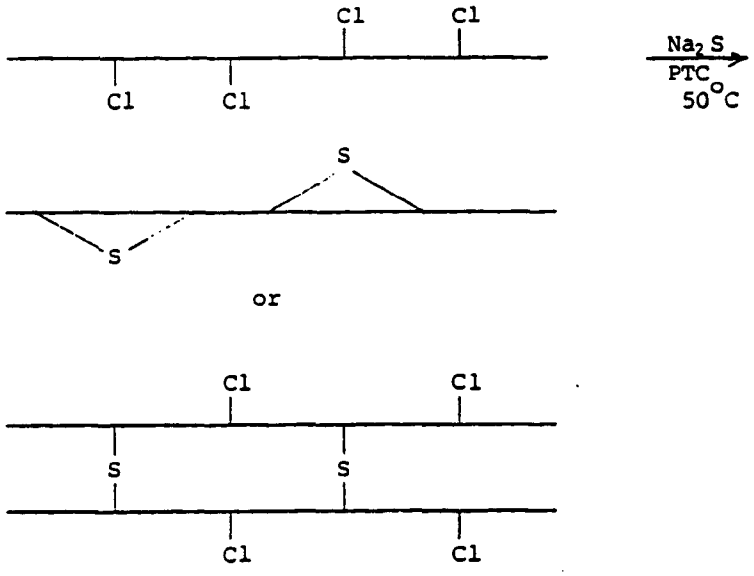
These indicate a crystalline phase change. However, the T_1/T_2 test showed entirely different results, T_1 below 0°C, with T_2 of about 100°C; these results were from two different polymers including the one used in the DSC test.

The polymer  (4015D-80-142B) shows on DSC:

Second heat; start @ 0° - endotherms @ 120°C and 155°C with decomposition starting @ ~170°C.

The T_1/T_2 test shows a T_1 of about 45°C and a T_2 of about 120°C.

The action of aqueous Na_2S on THF solutions of various chlorine containing polymers is also being studied. I feel the liable Cl's can be made to react with Na_2S to give either ring containing polymers or crosslinked ones:



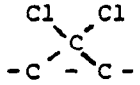
Polymer	Results
PVC-2 grades	No color change, soluble
CPVC-BFG	Dark brown, gelled rapidly
CPVC-Nippon Carbide	" " " "
CPVC-Parker-lightly chlorinated	Dark red-brown, gelled
" " 64% Cl	" " "
" " 70.5% Cl	" " "
Geon 222, 27% VCl_2	Dark purple, gelled rapidly
Chlorinated CB, 54% Cl	No color change, gelled
Halodenes - various levels of reaction	" " " , no gelling.

Five runs were made with PVC, using two different phase transfer catalysts and levels of Na_2S to 5 parts/100 PVC. The DSC results showed NO change in T_g (83-85°C). The TGA results, in N_2, likewise showed no differences in thermal stability.

The dark brown and purple colors indicate unsaturation, and the gellation indicates crosslinking and/or unsaturation also. However, IR results on the dark polymers do not show any indication of unsaturation. IR is not able to

detect the C-S-C linkage since it is a very weak IR band. Chlorine and sulfur analysis values are not available as yet.

Exactly what the reaction is between the polymers and Na_2S is now known. The results do clearly show the  structure to be the reactive site. The stability

of the  grouping in the Halodenes, is in keeping with previous obser-

vations.

Disclosure sheets have been written on the phase transfer condensation reactions.

Low Melting Glasses as Smoke and Fire Retardants: (Project 4016A-80) R. E. Myers -- Last quarter I emphasized the role of char formation as it relates to flame/smoke retardance of organic polymers. I indicated that our study of char promoting, intumescent systems has developed from our previous work on low melting glasses. The goal of our work is to develop effective inorganic-based flame/smoke retardants for a variety of organic polymers.

Our recent discovery of the ammonium pentaborate (APB) system is significant because it illustrates the potential flame/smoke retardant value of a simple, low cost, inorganic compound. In polyurethanes, such as Estane, we have shown that APB has a dramatic effect in reducing overall flame spread. A 1/8 inch thick sample of Estane containing APB will withstand at least 10 minutes exposure at 1000°C without sustaining backside damage to the polymer. A research report describing our preliminary work on APB will issue next quarter.

This quarter we have investigated the performance of APB in phosphate plasticized PVC. We have found that APB by itself does not have an appreciable effect in such formulations. However, during this study we did discover an effective flame/smoke retardant for phosphate plasticized PVC. By using a melamine molybdate/ammonium pentaborate system at 25 phr (total additive concentration) in a PVC recipe containing 50 phr of plasticizer, we observed increases in backbone char of up to 400% with a concurrent smoke reduction of 50%. The systems process well and produce a flexible sheet. By replacing a portion of the melmo with the less expensive APB, we have extended the melmo to produce a more cost-effective material. Studies are in progress to determine the performance of melmo/APB in the more conventional DOP-plasticized PVC.

This quarter we have investigated a novel phenolic resin-based system which, on the basis of preliminary data, serves to promote char formation and reduce smoke in phosphate plasticized PVC. The phenolic resin is a non-toxic material derived from a natural, i.e., renewable resource. The resin shows an effect at the 10 phr level in a PVC formulation containing 50 phr of plasticizer. I became interested in this phenolic resin, because I felt that it had the potential to generate an in-situ chemistry in the presence of a phosphate plasticizer. During combustion the plasticizer and the phenolic resin may be involved in a transesterification reaction, the net result of which is to provide a crosslinked phosphate plasticizer matrix. The physical manifestation of this process appears

in the increased char yields which are experimentally observed. Model experiments (suggested by Paul Nicholas) are in progress to test the proposed mechanism. We have also found that by combining the phenolic resin with our melmo/APB system, it is possible to attain smoke reductions of 55% with concurrent increases in char of ~500%. An invention record has been filed on this work. Future work will involve testing of the phenolic resin in DOP-plasticized PVC.

DOP-plasticized PVC represents a difficult system with respect to flame/smoke retardation. Smoke is generated not only by the PVC component but also by the DOP. Previous BFG work on plasticized PVC has shown that smoke retardants act only on the PVC component. In analyzing our low melting glass/DOP plasticized PVC systems, I have now found what may be the first example of a smoke retardant which acts on both the PVC and the DOP. The implications of such a finding are significant in that we may be close to identifying a highly effective smoke retardant for plasticized PVC. Future experiments will determine the reproducibility of this result.

Applications for Molybdates: (Project 4016H-80) W. J. Kroenke -- Our initial attempts to make K_C melamine molybdate more cost-effective by supporting it have been unsuccessful. Although we have been able to form a molybdenum compound on the surface of mineral supports, it does not appear to be K_C. And, relative to K_C, the supported materials are poor smoke retarders for PVC. They also do not interact synergistically with copper oxalate.

In order to see if our original idea has merit, we are switching to soluble amine molybdates. These molybdates can be directly applied to the surface of a support. They do not have to be prepared in place.

Bob Lattimer and I have started to study the character of the chars formed from PVC containing SS-50 and related copper and molybdenum smoke retarders. We hope to gain additional information about the role of the smoke retarders.

Our initial emphasis has been to prepare chars under combustion conditions and identify the fate of the metal additives in the chars. We have compared the weakly synergistic MoO_3-Cu_2O system with the strongly synergistic K_C-CuOX (copper oxalate) system (SS-50).

During combustion, MoO_3 decomposes differently from K_C, and Cu_2O differently from CuOX. However, in both cases the chars from the synergistic mixtures appear as simple admixtures of their respective component chars. That is, no new compounds appear in the chars from the samples containing the synergistic mixtures, which are not present in the chars from the samples containing the individual components. Additional work is in progress to understand these results and relate them to understanding the nature of the synergism in SS-50.

Chemical Intermediates from VCl and Polychloroethylenes: (Project 4022G) P. P. Nicholas -- This quarter, I completed two literature surveys. One covered the subject of this project, i.e., organo-transition metal catalysis that might apply to the conversion of VCl and related chloroethylenes into useful chemical intermediates. The second dealt with organo-transition metal catalysis for oxygenating olefins to epoxides with atmospheric oxygen-chemistry that mimics certain monooxygenase enzymes. I have recommended the former as my major 1981 program. The main reasons for this choice include: (1) BFG's current and future

leadership as a large volume, low cost VCl producer and the importance of this business to our future, (2) Our ability to use by-product HCl, (3) the potential for wider application of successful technology in upgrading certain chlorinated by-products. In general, I believe that BFG is in the best position to exploit practical developments in this area. Moreover, the favorable technical promise for this study suggested by certain reports in the scientific and patent literature is still another plus.

My program will begin with a study of amidation, i.e. the conversion of VCl to acrylamides by substitution of chlorine with an amido group $(-\overset{O}{\overset{\|}{C}}-NR,R_2)$. This group will originate from carbon monoxide and an amine during the reaction. The raw materials cost for such a process appears favorable based on the current selling price of acrylamide, itself. The catalyst study will begin with bis-(triphenlyphosphine)palladium II dichlorides of the general structure $Cl_2Pd[P(C_6H_4X)_3]_2$. It should be possible to assess the response of this reaction to both electronic and stereochemical effects at Pd(II), depending on the nature and position of the substituent, X. This quarter, I began the synthesis of these complexes.

New Methods for Producing CPVCs: (Project 4025F-80) Part 1 -- R. G. Parker -- Last quarter we produced high chlorine, high T_g CPVCs for study by B. L. Lee (see Part 2) and M. H. Lehr (see Part 3). During the Fourth Quarter, work was begun on the installation of the Hastelloy pressure reactor for use in the High Liquid Chlorine Process studies (with the Chemical Group). This reactor will be capable of producing pound quantities of highly chlorinated resins.

We have begun to understand the ^{13}C nmr spectra of CPVC much better, although the problem is far from solved (with R. A. Komoroski, Corporate Technical Support). By studying a lightly chlorinated CPVC chlorinated in solution, we know that the first detectable structural sequence formed in CPVC is -CHCl-CHCl-CHCl-. Further, this sequence also appears to retain the tacticity information present in the starting PVC sequence. To substantiate these conclusions, we are currently studying the nmr spectra of two vinyl chloride-1,2-dichloroethylene copolymers which should contain the same sequences (with R. H. Backderf, Chemical Group). The first sequence which appears to contain a CCl_2 carbon is $-CH_2-CCl_2-CH_2-$.

These nmr results have convinced us that it is no longer sufficient to describe the structure of CPVCs in terms of a polymer produced from the monomer units $-CH_2-CHCl-$, $-ClCH-CHCl-$, $-CH_2-CCl_2-$, and $-ClCH-CCl_2-$. Rather, the sequence distribution must be described in terms of five (or seven) carbon sequences (including stereochemistry). For a "normal" CPVC, there are about 77 probable sequences. A report was issued describing a new nomenclature system for use in describing the structural sequences present in CPVC (and other chlorinated polymers).

Work continues on developing the syntheses of isotopically labelled vinyl chloride from ^{12}C-carbon dioxide and ^{13}C-acetaldehyde. The PVCs which will be obtained will be used in our chlorination studies, and in PVC pyrolysis studies (W. J. Kroenke, Project 4016H-80).

Part 2 -- B. L. Lee -- Most polymer processing operations involve moving and shaping a polymeric material in the molten state, and then cooling it "rapidly" to the solid state. Basically, this process involves material response under conditions of simultaneous deformation and temperature change. I have recently found that under appropriate conditions, significant changes in the mechanical properties of blends of CPVC/PVC can be achieved by rapidly quenching stressed material from the rubbery state. Specifically, the experiments were performed using the Instron Capillary Rheometer. The blends (75/25 with 3 phr of T-31 stabilizer) were extruded through the die slit at 205°C. The extrudates were either subjected to on-line stretching, or no stretching. The Instron Tensile Test results indicated that the toughness and yield stress of the stretched material is drastically improved. These results suggest that it is possible to improve the toughness of CPVC using PVC, and no rubber modifier.

Part 3 -- M. H. Lehr -- We reported earlier that lightly chlorinated CPVCs (LCPVC), prepared in liquid chlorine, showed markedly reduced recrystallization in fused samples containing 60-61% chlorine. We discovered later that resins prepared by the water slurry process also showed the same characteristic. We speculated that reduced crystallinity in LCPVCs might make possible the blowing of low-density vinyl foam, and the development of easier processing compounds.

Laboratory rheological tests confirmed the expected benefits of reduced crystallinity in LCPVC. Tests were made on PVC (Geon 103EP) and LCPVCs (59-62% Cl). The LCPVCs were made from the same Geon 103EP by both thermal and photochemical initiation. The resins were made into compounds containing 2 phr T-31 stabilizer and 0.5 phr PE lubricant only so that the inherent resin properties could be measured.

Instron rheometer results showed the apparent viscosity of PVC was more pressure sensitive than that of LCPVC. The pressure required to extrude PVC increased curvilinearly with die L/D ratio at 300 sec^{-1} at 170°C and 200°C. At an L/D of 40, the pressure required to extrude PVC was increasing steeply, and was significantly greater than that needed to extrude the LCPVCs. In contrast to PVC, the LCPVCs showed a linear relationship between pressure and L/D ratio.

PVC and LCPVC do not exhibit the same viscosity behavior. Apparent viscosity versus shear rate curves (Instron rheometer), and complex viscosity versus frequency curves, were steeper for LCPVC at 200°C. This shows that LCPVC was becoming more fluid than PVC at the high shear rates. This result suggests that LCPVC would flow more easily than PVC during injection molding.

PVC and LCPVC showed about the same die swell (>150 sec^{-1}) at 170°C where particle flow would be expected. However, at 200°C, where melt flow occurs, PVC showed greater die swell than LCPVC.

This work has been reported to the Chemical Group at a Project Review and an Exploratory New Products meeting. Effort is now underway to prepare large samples of the LCPVCs at the ALTC pilot plant. These resins will be tested by the Chemical Group in foam, extrusion, and injection molding applications.

Reaction Zone Theory and Its Application in the Development of Water Chlorination CPVC Processes: (Project 4025G-80) G. S. Huvard -- During the fourth quarter, I've characterized rates of HCl vapor diffusion in PVC, supported original Cl_2 vapor diffusion rate estimates, demonstrated that pore diffusion effects can alter rates of PVC photochlorination and shown that morphology of suspension and mass resins can have an enormous effect on chlorination rates and resin properties. We have also shown that Cl_2 uptake rates and HCl loss by diffusion are much slower in H_2O slurry systems than for simple vapor phase experiments. Both of these observations require in-depth study as they affect rates of chlorination, resin properties and neutralization rates.

To be more precise, HCl diffusion coefficients from 30°C to 60°C are given by:

$$D\frac{cm^2}{sec} \simeq 0.68 \exp\left(\frac{-12200}{RT}\right)$$

The diffusivity at 30°C is in agreement with Berens' correlation for numerous penetrants in PVC at 30°C while the activation energy, 12.2 kcal/gmol, is in agreement with data given by Tihkomirov for activation energies for diffusion in PVC versus penetrant diameter.

Chlorine diffusion times in vapor phase experiments are in agreement with expectations based on Berens' and Tikhomirov's correlations. These rates are much faster than times observed by Parker for Cl_2 uptake in PVC slurried in H_2O. We believe this is a manifestation of pore diffusion limitations and not bulk phase to PVC surface mass transfer resistance.

A dramatic effect of PVC particle morphology has been demonstrated with the help of Bob Schlegel (Chemical Group CPVC). We compared chlorination rates of standard 103EP suspension resin with reprecipitated 103EP having a drastically different morphology (much higher specific surface area). Reaction rates for these two were comparable yet the reprecipitated resin had better apparent heat stability. We repeated these experiments using 110x236, a resin which has very poor water chlorination rates and gives very poor CPVC. However, when reprecipitated to a high surface area morphology, 110x236 has rates faster than 103EP and apparently comparable heat stability. These two experiments dramatically demonstrate that evidence exists to support both intrinsic rate control as well as diffusion rate limitations to chlorination rates.

Future work will be centered on separating and understanding the diffusion and intrinsic rates that occur during photochlorination and the interaction of these factors with Reaction Zone Theory. We are beginning an in-depth study of morphology effects on Cl_2 diffusion rates in PVC and CPVC water slurries. The Chemical Group has approved funding for a microplant system utilizing a controlled photoillumination reaction zone. This system is expected to be on-line by middle or late summer of 1981.

A research report covering the theory of photochlorination, the Reaction Zone Theory, diffusion related theory and initial Reaction Zone experiment has been completed and will be issued very shortly. I would urge all parties involved with PVC chlorination to read this report, formulate new and/or criticize old theory and report your ideas at Chlorpig meetings.

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Organics and Plastics for Photovoltaic Systems: (Project 4027G-80) L. Traynor -- We have continued to work on promising avenues in solar cell fabrication. I believe we can reproduce cells giving about 0.1 volt and 2 μamp/cm^2 photo-outputs. These are cells made using a) electron donor additive, b) heat treatment and c) dichloroethane/2-methoxyethanol spin casting solvent. Approaches a) and b) were suggested by our work using narrow band pass filters. We need to optimize electron donor structures and try even higher temperature heat treatments. An important discovery this quarter is the mixed solvent system. A continuing problem in this research has been the poor quality of the spin cast films. Using cellulose acetate polymer binder with the mixed solvent, we can obtain very good pinhole free films. There appears to be dye aggregation although macroscopically the films are uniform. I feel we have positive directions in which to proceed although progress is slow.

We have continued to investigate polypyrrole as an inherently conducting polymer. We have synthesized several N-substituted pyrrole derivatives. Only with the N-butyl derivative were we able to obtain a film suitable for conductivity measurement. Conductivity of this film was 4 orders of magnitude lower than polypyrrole itself. We have been able to make films using a comonomer mixture of pyrrole plus N-substituted pyrrole. Conductivity of these films is a little lower than polypyrrole. We have two of these films submitted for reflectance infra-red and Raman spectra to look for evidence of comonomer incorporation into the polymer film.

The polypyrrole films are made by oxidative electrodeposition of pyrrole. We can easily measure the voltage applied to the electrolysis cell. The table shows the effect of applied voltage on the film conductivity. Clearly (and we have seen this in other series), the higher applied voltages give higher conductivities. Attempts to measure actual electrode voltage are in progress. We

Film No.	Applied Voltage	Film Conductivity
869-1	10 volt	25 $ohm^{-1}cm^{-1}$
869-2	5	18
870	2.5	3

will continue to explore variations in electrolysis conditions as well as other pyrrole derivatives and related compounds.

Polymers with Thermally Reversible Linkages: (Project 4028K-80) F. L. Ramp and L. F. Stiberth -- This project remains in a highly exploratory phase. Thermally reversible bonds in the main chain and optionally in crosslinks should give a polymer with metal-like melt behavior, i.e. from rigid to very fluid. Two types of bonding linkages are under investigation: (1) the Diels-Alder reaction and (2) compounds which break reversibly to stable radicals. Diels-Alder approach: Furan compounds offer a wide variety of materials for the diene component. However, a literature study of furan in the Diels-Alder reaction is not encouraging. This approach has been set aside at this time. Anthracene offers a stable but reactive diene system. However, studies to date have not uncovered a satisfactory method of incorporating two or more anthracene structures in a compound. The latest approach, copolymerizing anthracene as a diene under free radical conditions, did not support earlier literature reports. This approach is still being studied. Bond cleaving to stable radicals: Compounds

which have a carbon with electron donating and electron with drawing groups on the same carbon give stable radicals. Aminonitriles such as those derived from the Strecher synthesis possess the desired structure but lack hydrolytic stability. 2,3-Diphenyl succinonitrile has been prepared with the object of closing a ring putting amino groups on the 2,3 position. The compound has proven to be very inert to attack at these benzylic positions. However, tetraphenyl succinonitrile breaks to oxygen stable radicals readily. The 2,3 diphenyl will be checked for radical production. A paramethoxy group should increase radical stability and can be easily incorporated.

Bloom in Polymers: (Project 4028L-80) F. L. Ramp and L. F. Stiberth -- Work on this project by the authors has previously been reported under Project 4028K. The results to date are covered in detail in a status report. Briefly we have shown that sulfur bloom is due to supersaturation. DSC can be used to determine whether the rubber compound is taken from the last mastication above the critical bloom temperature. Stocks allowed to cool from above the critical bloom temperature, without mixing, will supersaturate and bloom.

Bloom of zinc stearate has been shown to be caused by different factors. Zinc stearate bloom forms in two distinct manners with different driving force for the bloom. These two phenomena are conveniently categorized as: (a) thermal bloom and (b) high humidity bloom.

Thermal bloom develops very rapidly on stocks above the melting point at the last mastication. This bloom is readily controlled by insuring that the stocks are cooled below the "zinc stearate" melting point in the last mixing.

High humidity zinc stearate bloom develops over a period of hours or days at 50°C and ~90% humidity. Data to date indicate that this bloom is due to the conversion of zinc stearate - form II (see the status report) to the more stable zinc stearate - form I. The main focus of current efforts is to confirm these observations and to develop suitable preventative measures.

Rubber-Plastics Composites: (Project 4041B-80) G. S. Huvard -- EPG's Les Fox was brought up-to-date on the composites reported last quarter. The properties of PE/scrap rubber composites and expected costs make these materials possible candidates for roofing membrane materials. I encouraged Les to consider this approach in his up-coming studies in this area. Further work has been suspended pending EPG's response. If favorable, I offered Les help in formulating and testing membranes made from such composites.

PROCESSING RESEARCH

Improved Rubber and Plastics Processing: (Project 4010B-80) V. L. Folt -- Our objective remains the determination of the optimum molecular weight and branching distributions required in our commercial polymers to optimize processing rates and product properties while minimizing energy consumption in processing operations. In the pursuit of these ends we are studying the viscoelastic and rheological properties of blends of linear and star-branched polybutadienes.

In the last quarterly report, we discussed the melt viscosity behavior of blends of various branched polymers with a specific linear polymer. Although the intrinsic viscosity values for the blends increase linearly with an increase in the weight concentration of the branched component in the blend, the melt viscosity increases in a very complex manner with increasing branch concentrations. And, the melt viscosity is also observed to increase linearly with increasing intrinsic viscosity but, on a log-log basis. There may be a critical branch concentration, depending on the branch length, at which the slope of the line changes abruptly.

In all previously reported blend systems, the intrinsic viscosity of the branched component was higher than that of the linear component. We have now completed a study of a blend system in which the intrinsic viscosity of the branched polymer was lower than that of the linear component. In this case, the melt viscosity of the blend was observed to decrease linearly as a function of the intrinsic viscosity on a log-log basis, while the melt viscosity increased, again, in a complex manner, as the concentration of the branched component increased.

We also studied the behavior of a blend system in which the intrinsic viscosity of the branched component was virtually identical to that of the linear component. Here we observe that the melt viscosity of the blends ranges from that of the branched polymer to that of the linear polymer, all at one specific value of the intrinsic viscosity. Simultaneously, there was a tenfold increase in melt viscosity observed as a function of increasing branch concentration.

We have also prepared blends of linear and linear fractions. Preliminary data clearly demonstrate that linear-linear blends behave significantly different from branched-linear blends of comparable intrinsic viscosity values. We are now about to extend the study to include blends of branched molecules with branched molecules. We hope, here, to clarify behavior differences between these due to branching from those due to variation in molecular weight distributions.

In view of the type of results we are observing, it has become imperative that we have accurate molecular weight data to properly interpret our results. Dale Harmon is applying laser light scattering techniques to attempt to measure the weight average molecular weights of our polymers used to prepare the blends. Data obtained on our linear polymers stand in agreement with literature values for polymers of comparable stereoregularity and intrinsic viscosity. Work is now in progress using our branched fractions.

Alloys as the Basis for New CPVC Compounds: (Project 4018C-80) M. H. Lehr -- The Hi-Temp group is planning a test program to evaluate phosphate, phosphite, and citrate salt co-stabilizers in Hi-Temp pipe compound. We discussed with them our citrate stabilization technology, which we developed initially for CPVC/polyester alloys. We have also shown that Na^+ and K^+ citrates are effective co-stabilizers in Hi-Temp compound. In addition, we showed how an anti-oxidant improves the stability of Hi-Temp compound. For example, .4 phr of Ethyl 702 or Goodrite 3125 afforded a 50-100% increase in Brabender stability time, depending on whether the CPE modifier was fused with the other ingredients or added later. The more stable compound was obtained when the CPE was added later after the other ingredients had banded on the mill. We also presented evidence that getting good stability may depend on equipment factors. When we mixed our compounds in the Banbury at ALTC (with CPE present initially or added later) the benefit of AO was not realized.

Process Innovation: (Project 4045A-80) J. Sidles and J. J. Blayne, Jr. -- We continued work on extruder blended curatives to achieve fast curing extrudates. Plans were finalized with Tire Development to build additional farm tires in the Miami, Oklahoma Plant, first quarter, 1981. This will yield additional tires for field testing. It will also enable an assessment of this system under factory conditions, using production size extruders.

In other work, we showed that press-cured passenger retread tires using the "Fast Cure" approach could be cured in 40% less time than conventional compounds and methods. This work was undertaken to support Tire Group efforts aimed at licensure of the process to the retread industry.

Work on ventless molding of passenger tires was continued. We evaluated a steam injection mode based on injection through small holes in the lower half of the mold. The steam was injected radially inward during the press pause just before total closure. This yielded the best looking tires to date, and will form the basis for a new, production size ventless mold now on order by Tire Development. Our plan is to try this mold at Brecksville, then place in pilot production at the Ft. Wayne Tire Plant. A Tire Group financial analysis shows a potential discounted cash flow return of 59.9% on an investment of $1.8 million, and an annual savings of $1.7 million.

PRODUCT PERFORMANCE RESEARCH

Diffusion in Polymers: (Project 4002A-80) A. R. Berens -- Our previous vapor sorption studies of PVC indicated that an unusual "dilated" structure may result from exposure of the polymer to a swelling vapor, followed by rapid removal of the vapor under vacuum. We have renewed investigation of this process to learn whether it may be applicable to PVC films, as well as powders, to produce potentially useful modifications of properties. Treatment of PVC resin with methyl chloride vapor, at room temperature and pressures above atmospheric, produces the "dilated" structure, as evidenced by increases in sorptive capacity and the appearance of a sub-T_g endotherm in DSC curves. Unsuccessful preliminary attempts to produce this effect in a rigid PVC film have prompted a systematic experimental and theoretical study of the effects of vapor exposure and thermal history on the calorimetric (DSC) properties of PVC, now being carried out and reported under Project 4002G (see below). This study is helping to define conditions for producing the "dilated" structure and to predict its physical properties.

In the continuing work on PVC particle-structure characterization through sorption kinetics analysis, the histographic distribution approach developed for gravimetric data is being applied to gas chromatographic sorption and desorption data. Gary Huvard has extended the computer program to calculate GC curves from known particle size distributions, and conversely. Experimental GC curves agree satisfactorily with the calculations for both sorption and desorption runs with MeCl on microsuspension PVC's. These results support our earlier suggestions that the "VCM desorption test" could be made more versatile by employing different vapors for various particle size ranges, and less time-consuming by operating in the sorption mode, instead of desorption.

Vapor-Induced Relaxations in Glassy Polymers: (Project 4002G-80) I. M. Hodge and A. R. Berens -- This new project covers the research being performed at Brecksville under National Science Foundation Grant No. CPE-7920740 to BFGoodrich and North Carolina State University, part of NSF's Industry/University Cooperative Program. The overall objectives of this basic research project are to apply vapor sorption procedures for producing and monitoring relaxation processes in rigid polymers, and to correlate results of sorption studies with thermal, mechanical, and dielectric techniques more conventionally used to study polymer relaxations.

A major part of our proposed research involves the study of dielectric relaxations in polymers containing, or previously exposed to, penetrant vapors. Exploratory "dielectric creep" experiments, using equipment on hand, have demonstrated that meaningful data can be obtained on porous discs formed by cold-pressing PVC powder; DC discharge currents show the anticipated shift toward longer relaxation times during annealing after a thermal quench. We have surveyed the requirements and capabilities of available equipment for both time-domain (dielectric creep) and frequency-domain (AC dielectric loss spectroscopy) measurements on polymer films and powders. An AR is being written for acquisition of equipment which will be of general value in BFG corporate and divisional R&D programs, beyond its immediate applications in this project.

Most of our attention this quarter has been directed to an experimental and theoretical study of the effects of vapor exposure and thermal history on the calorimetric properties of PVC (cf. Project 4002A):

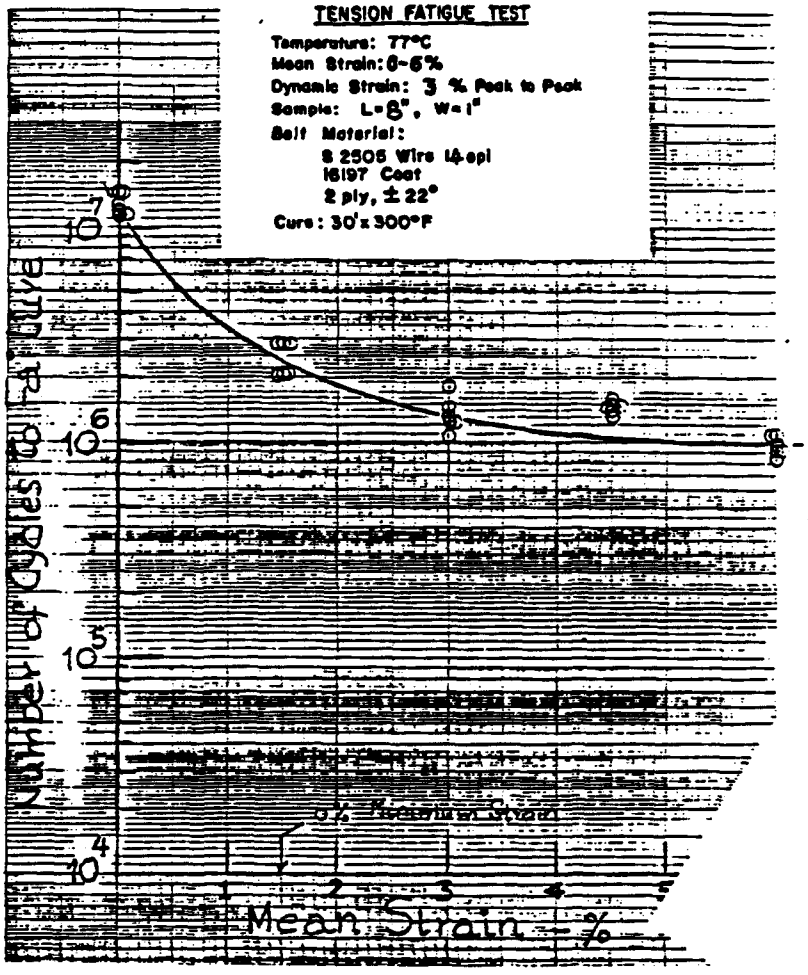
Experimentally, DSC curves have been obtained for PVC samples which were exposed to varied pressures of MeCl vapor, or thermally quenched at varied rates, and subsequently aged at varied temperatures and times. Development of a pronounced sub-T_g endotherm, growing with aging time and shifting to higher temperature with increased aging temperature, is observed for the vapor treated samples and for the most rapidly thermally-quenched samples (plunged into liquid nitrogen from 120°C).

The parallel theoretical study involves a mathematical relaxation model which contains parameters expressing the non-exponential rate of relaxation (due to a distribution of relaxation times) and its non-linearity (related to the dependence of relaxation rate upon free volume.) A computer program based on this model can simulate a DSC experiment and predict the general effects of varied thermal quenching and annealing history. This program has successfully modelled all of the major effects observed experimentally. We may tentatively conclude that the development of a sub-T_g endotherm, like the more familiar "T_g overshoot" endotherm, is a consequence of enthalpic relaxation occurring during the prior aging period. The early and magnified appearance of this endotherm during aging, even near room temperature, suggests that vapor exposure, like a very rapid thermal quench, produces sufficient "frozen-in" free volume to allow unusually rapid and pronounced relaxation. Further application of the model and computer simulations, coupled with experimental DSC data, seems to hold real promise for prediction of long-time aging effects on polymer physical properties from short-time laboratory data.

Design of Composite Products: (Project 4004A-80) M. K. Chakko -- The objective of this project is to achieve better scientific capability for designing our cord-rubber composite products. In our study of the fatigue behavior of tire belt composites, the main loading parameter has been the dynamic amplitude of the extensional strains applied to the belt samples. This quarter we investigated the effect on fatigue life of changing the mean strain level. The data obtained for 3% peak to peak dynamic strain amplitude with mean strain varying from 0 to 6% are shown in the figure. The fatigue life decreased as the level of mean strain was increased. As in the previous tests, the separations and failure occurred in the interply rubber, which in these samples was mostly natural rubber. Yet, the decrease in fatigue life with increasing mean strain (or minimum strain) was observed. At the levels of mean strains below 1.5% in these tests, the samples were subjected to compression and buckling. The fatigue life, however, was higher. This may be due to the fact that the critical interlaminar shear strains at the edge of the samples remain near zero when the sample buckles, thus reducing the actual dynamic shear strain amplitude in the test.

The fatigue testing conducted so far was mostly on steel belt composites. Currently, we are evaluating the fatigue characteristics of Rayon belt composites. Results to date show that the Rayon belt composites are superior to the steel belt composites in edge separation resistance.

Using the new MTS Automated Dynamic Test System, we have measured the viscoelastic properties of rubber under non-sinusoidal deformations. For deformation wave forms we used triangle, Sine and a rectified Sine similar to



those occurring in tires. Differences in energy loss per cycle were observed among the different waveforms. In the case of the rectified Sine waveform of deformation, the elastic modulus was up to 25% higher than the sinusoidal value.

Fiber Reinforced Plastics Composites: (Project 4006G-80) M. L. Dannis -- The information on creep characteristics (at room temperature) has been written up in a research report now almost ready for release. As the whole set of data was considered, several premature "conclusions" had to be revised. At the moment, the early part of the creep curve seems to fit the Andrade equation.

$$E(t)/E_i = t^{-n}$$

This is a curve-fitting expression, without important meaning related to creep itself as a molecular phenomenon. However, it does provide a useful comparison of initial modulus value E_i and of n (the log-log slope) in families of related materials. It must be emphasized that this Andrade relationship covers only

particular ranges of the much wider relationships discussed by John Ferry and co-workers, i.e. the W-L-F shift concepts.

The various relationships discussed in the report show the importance of extending the range of the creep data in both time and temperature. A six station creep assembly is being built to do just that.

On the practiced side, a glass fiber reinforced Estane made at ALTC had a surprisingly high initial modulus, attained without major damage to the fiber loading. This has some possibilities as a sheet molding compound, but would be almost worthless for injection molding. The difference lies in the moderate reshaping of the SMC compared to major fiber destruction during injection molding. Further work is needed to advance this concept and to establish a preliminary cost-value relationship.

Low Combustibility Technology: (Project 4007G-80) E. D. Dickens, Jr. -- I completed an initial evaluation of LDF foams being made by EPG (R. Srail). The foam tested was ~1.8 lb/ft^3 density. Its smoke was very low and in line with values expected for the starting polymer. Efficiency of char formation was ~60% for the foam as compounded versus ~75% for the un-blown compound. The foam shrank drastically when exposed to a flame and lost most of its weight (as HCl). A glow problem was observed and is believed to be due to the use of TiO_2 in the compound. Possible solutions, based on recent work by A. McRowe, Chemical Group, were suggested to EPG and are currently being evaluated.

High Performance Polymer Bonded Ferrite Magnets: (Project 4020B-80) J. J. Blayne, Jr. -- The 400 lb. run of Hycar 4001 rubber from Avon Lake was received in early October. This material was tested and found to be equivalent to the lab samples that we had tested earlier.

A factory trial at Marietta was planned for October 21. At the plant, a series of compounds from 55 to 70 volume percent ferrite were mill mixed, granulated, extruded, magnetized and tested. The results of this trial were very encouraging and the significant results were:

1. The Hycar 4001-AC540 binder system milled very well and accepted the BG-2 powder faster than the present Hypalon-Vistanex system.

2. The Hycar 4001-AC540 binder system extrudes at significantly lower head pressures than the production compound.

3. The highest loaded experimental compound (≈69 volume percent BG-2) equals or exceeds most specifications for a gasket grade material.

4. The excellent thermal stability of the Hycar 4001 allows a wide range of extrusion temperatures (≈280-400°F).

This successful factory trial has encouraged the Marietta technical staff to proceed with investigation of this new binder system. Additional consultation and experimentation will be provided as needed.

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Work has now resumed on the High Strength Magnetic compound based on Hycar 4001, AC540 and HM130. Initial experiments will determine optimum temperatures for extrusion using the existing four piece die. This will be followed by compound optimization for the highest magnetic strength with acceptable processability. Work on die design variables will proceed concurrently.

A factory demonstration of the high strength magnet technology is planned for the near future.

E. D. Dickens, Jr. -- In order to provide technical guidance to the extrusion trials and compounding program of Jerry Blayne, I have spent considerable effort in familiarizing myself with magnetic measurement techniques and repair of our hysteresisgraph. I feel confident in our ability to do and interpret these measurements. I have also made an effort (still ongoing) to pull together our past work on effects of volume loading and orientation.

At the request of Marietta technical, I looked into the area of microwave ferrite gaskets. I have sorted out most of the basic physics used in this application. The ferrites used are not the type currently used by Marietta but are in fact specific "soft" ferrites tailored in composition to have an adsorption maxima at ~2.5 GHz. I have received samples of potential powders from Ceramic Powders and they can be milled into current binders. At the request of Marietta technical and magnetic marketing, I talked to technical staff members at Hardwick Stove and Magic Chef to clarify the situation with respect to samples of our current magnetic gasket material submitted to them earlier this year. In all cases, our current material was found to be ineffective (an expected finding). The more technical sound customer (Magic Chef) is looking into patents a literature search found that TDK (Japanese) has on this type of gasket and its use in ovens. No further action is planned until this legal issue is resolved since TDK is the sole supplier of this product at this time. (The patent situation has been reviewed with Bob Lindsay of the Legal Staff).

Our successful extrusion trial of gasket grade magnets at Marietta (see above) pointed out a key difference between extrusion at Marietta and Brecksville. The extruders used in magnetic production operate in an almost adiabatic fashion. This means that the highest loaded compound generated a high stock temperature due to shear heating and this higher stock temperature offset a lot of the viscosity increase due to the higher filler loading. The remarkable thermal stability of Hycar 4001 allows us to take full advantage of this feature. I have worked out quite reasonable models for the extrusion processes at both Marietta and Brecksville that take into account the effects of filler loading and the type of heat transfer involved (adiabatic vs. isothermal). The models clarify key issues involved in obtaining large increases in production output while giving at the same time a potentially large decrease in wear on existing equipment. The same type of strategy is being used in our work at Brecksville on the high strength magnet phase of this program.

Optimizing the Performance of Rubber Blend Products: (Project 4029A-80) B. L. Lee -- Most rubber products are blends of two or more elastomers and several additives. The objective of this project is to develop new technologies that will enable our operating groups to optimize the performance and cost of rubber blend products.

We have reported that in the SBR-CB tread compound, the hysteresis can be reduced by selecting the carbon black distribution in the individual SBR and CB phase. Most recently, we studied the hysteresis by selectively locating different types of carbon black in the SBR and CB phase. The preliminary study is on 19955 compound, a low rolling resistance compound. The carbon black is mixture of N650 (coarse particle) and N234 (fine particle), with 36% of N650. The results indicate that the hysteresis can, indeed, be reduced. Adding the coarse particle to the CB and the fine particle to the SBR would reduce hysteresis. However, abrasion resistance is reduced too. Adding the coarse particle to the SBR and the fine particle to the CB phase would minimize the loss of abrasion resistance due to the presence of coarse particle. The unvulcanized properties based on Dynamic Stress Relaxometer show marked difference in viscosity and stress relaxation behavior. This might affect die swell. We are planning to study the extrusion behavior.

Plasma Polymerization: (Project 4030A-80) - No report this quarter.

Conductive Composites: (Project 4032C-80) - No report this quarter.

Adhesion Science: (Project 4039A-80) D. B. Rahrig -- The bonding of rubber to synthetic cord materials is achieved with resorcinol-formaldehyde-latex (RFL) adhesives. One of the primary goals of this project is to understand the interrelationships which exist among the chemistry, morphology and mechanical properties of RFL systems and how these interrelationships impact adhesion.

In the last two quarters, we have reported on the use of the Dickie equations to predict the dynamic mechanical response of RFL films. Acknowledging the fact that RFLs are two phase systems, and assuming that the RF resin forms the continuous phase, one can predict the effect of a changing latex/resin ratio on the complex modulus and tan δ behavior of RFLs using these equations. The experimental results suggest that for RFL films cast at 65°C and having ammonia in the recipe, the resin phase is continuous for latex/resin ratios of up to 20/1. For heat treated RFLs or those prepared without ammonia, however, the continuity of the resin phase appears to breakdown at lower latex/resin ratios. The results are summarized here:

Sample	Latex/Resin Ratio Above Which Resin Continuity Breaks Down
RFL with ammonia	
as cast	>20/1
pressed @ 175°C	8/1
air cured @ 220°C	5/1
RFL without ammonia	
as cast	10/1
air cured @ 220°C	10/1

Thus through dynamic mechanical experiments and the use of the Dickie equations, we have been able to learn details of RFL morphology which are beyond the resolving power of electron microscopy.

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This morphological information appears to be applicable to understanding adhesive performance. Using two series of RFLs, one prepared with ammonia and the other without, and drying these adhesives on nylon at 220°C; we found that adhesion increased as the RFL latex/resin ratio increased. But for the RFLs containing ammonia, this trend stopped when the latex/resin ratio went above 5/1. And for the RFLs without ammonia, the trend stopped when the latex/resin ratio went above 10/1. Thus in both cases the trend of increasing adhesion with increasing latex/resin ratio stopped at the point where resin phase continuity is thought to breakdown. The RFLs prepared with ammonia also displayed a second adhesion maximum at the 12/1 latex/resin ratio, which is well above the level where resin phase continuity ends, however. The reason for this second maximum is not yet known.

Highly Filled Materials and Composites: (Project 4040A-80) I. M. Hodge -- No report this quarter.

Project LDF: (Project 4041C-80) G. S. Huvard -- During the fourth quarter, Dick Backderf (who performed the experiments) and I completed an assessment of F-11 diffusion rates and mechanisms of F-11 diffusion in LDF compound resins. Our latest compounds sorb F-11 athermally and, depending on temperature and thickness, will show both Fickian and Case II diffusion behavior. Based on our results, I successfully scaled a slurry sorption system to supply up to 150 lbm/wk. of F-11 saturated LDF compound cubes as a control feedstock for EPG's extruder and die design efforts. Ray Srail has developed a method for desorbing F-11 to give materials having the proper level of F-11 for extrusion. The technical interaction and progress on this project have been outstanding - Harry Ayres should have his extrusion designs optimized in the near future. We will continue to supply feedstock as long as is necessary.

The slurry sorption system may be a viable alternative to an F-11 injection process. To this end, a process synthesis and Rapid Cost Estimate will be drawn up before the end of January 1981. A research report covering the fundamentals of high activity F-11 sorption in LDF resin will be written during December and issued in January or early February.

RESEARCH PLANNING

Project Market Research: (Project 4026A-80) J. M. Marks -- In support of Project 4025F, I provided Marv Lehr marketing information on lightly chlorinated PVC. This information plus other technical information formed the basis for Marv Lehr's presentations at the Chemical Group's "Project Review" and here at Brecksville.

Finally, in support of Project 4020B, I collected information on the 1979 net sales, market contribution ($ and %) and pound sales on the "Bonded Magnets" business segment of the Fabricated Polymers Division of the Engineered Products Group. Doug Dickens used this information when he reviewed the chronology of the High Strength Bonded Magnets Projects for the Group Technical Heads program "Studies of the Innovation Process within BFG". I have also included this information in a report "Magnetic Business 'Profitability'", which was issued during the quarter.

Market Research: (Project 4026B-80) J. M. Marks -- During the quarter I completed and issued a report "Business Segment 'Profitability'". This report gives the 1979 net sales, market contribution ($ and %), and division contribution for all of the business segments of Chemical, EPG, and Tire. I have also completed and issued a report "The Solar Space and Hot Water Heating Market". The purpose of this report was to determine if there are opportunities for BFG in this emerging market. Further, I held a brainstorming session for a product which had been made earlier at the Research Center but had not gone commercial. The purpose of this session was to determine possible applications for this product, known as Memolastic, which has a special property, memory. The next step will involve screening of these applications to determine if further investigation is warranted. Finally, I have begun collecting information on the synthetic fuels industry in preparation for a presentation which I am planning to give to the Management Committee sometime in the first quarter of 1981.

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BFGoodrich

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The BFGoodrich Company
3925 Embassy Parkway
Akron, Ohio 44313-1799

January 11, 1990

Mike Easterling
Reneer Film Corporation
Rt. 895 West
Auburn, PA 17922

SUBJECT: GEONS 110X450, 110X500 and 110X911 - FDA STATUS

Dear Mike:

This is in response to our conversation regarding the FDA status of the above Geon PVC resins.

Geons 110X450, 110X500 and 110X911 are homopolymer polyvinyl chloride (PVC) resins. Polyvinyl chloride is prior sanctioned for use in general food contact applications, both flexible and rigid. The prior sanction is based on an article by A. J. Lehman, from the FDA, published in the Journal of the Association of Food and Drug Officials, July, 1951. The current Good Manufacturing Practice (GMP) specifications for prior sanctioned PVC are a maximum volatility of 3.0% (1 hour at 105°C) and an inherent viscosity of not less than 0.35 by ASTM D-1243-79. Geons 110X450, 110X500 and 110X911 meets the GMP specifications for prior sanctioned PVC, therefore meet the current requirements of the FDA for general food contact applications including food wraps.

PVC is also listed as an acceptable ingredient of food contact articles under 21CFR:

175.105	177.1200
175.300	177.2250
176.180	179.45
177.1010	

If you have any further questions, please call me at 216/374-3422.

Sincerely,

THE BFGOODRICH COMPANY

W. C. Bachtel

W. C. Bachtel
Toxicologist
Health and Environmental Services

91024-3/jp
cc: G. Schoff - CL-OTM-3

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