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THE COLLEGE OF AERONAUTICS

DEPARTMENT OF MATERIALS

Visit to America

September 11th - September 25th, 1967

- by -

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The first visit was to Chicago to attend the 154th meeting of the American Chemical Society and to give a paper in the Division of Organic Coatings and Plastics Chemistry. In fact the writer found most personal interest in this division (which was sub-divided into Sessions A and B) and this memorandum is confined to the activities of that Division. The papers are all available in book form and the accounts here represent the author's opinions and reflections on some of the papers. Numbers refer to the programme and the references are given. All page numbers refer to the ACS 154th Meeting in Chicago, September 1967, 27, No. 2.

Tuesday, September 12th

Section B. In papers 23 (W.R. Miller, et al. p. 160) paper 24 (L E. Gast et al. p. 168) and paper 25 (H.G. Nieschlag et al. p.174) descriptions were given of novel polymers prepared from monomers derived from natural sources. These were soyabean oil, crambe oil and linseed oil, dusocyanates being used in cross-linking processes. The interest here is that some of the raw materials are cheap (crambe oil 20¢/gallon).

Wednesday, September 13th

Paper 31 (C.K. Lyon and G. Fuller) p. 236 and Paper 32 (N.J. Monson and A.H. Albrecht) p. 239 were noteworthy papers on flame resistant urethanes and fluorochemical coatings. Both certain useful ideas and work.

The author's paper on the thermal degradation of epoxide resins was delivered in the afternoon (Paper 42, p. 321) and there was particular interest from Dr. Cohen, of the General Electric Co. Schnectady, N.Y. They have a considerable practical interest in epoxide degradations and changes in electrical properties during degradation. A copy of College Note Mat. No. 10 (J.C. Pattison-Jones and D.A. Smith) was given to Dr. Cohen and he promised to send reprints and correspond on matters of mutual interest. He showed some interest in the College and should be given relevant literature.

The Divisions social evening met and I was introduced to Dr. Alexander, Naval Research, Mr. Wall, National Bureau of Standards and Dr. Jellinek (Clarkson College of Technology).

Thursday, September 14th

A symposium was held by the Division on Polymer education, the initial item being a panel discussion. (Panelists W.J. Sparks, Consultant, Westfield N.J., R.W. Cairns, Research Director, Hercules Inc., Wilmington, Delaware, Prof. W.J. Bailey, Chemistry Dept., University of Maryland, Prof. C.G. Overberger Chemistry Dept., University of Michigan, Ann Abor).

There were complaints from the industrial side that not enough useful and practical polymer chemistry found its way into undergraduate courses.

Post-graduate degree students in polymers were recruited from chemical engineers largely, plus a few engineers. There was no shortage of graduate students, but it was felt unsatisfactory that so few pure chemists and physicists took higher degrees in polymers. Several speakers stressed the need for polymer science, i.e. physics and chemistry together, rather than having them segregated as is usually the case.

Papers 57-62 consisted of speakers from universities setting forth the nature of their courses, papers followed from industrialists mostly stressing the need for students in polymer science having graduate degrees.

Some particularly interesting studies appear to be going forward under Prof. E. Baer at Case-Western Reserve University, where pvc micro-spheres of 1000 Au diameter are being investigated. These are being used to make 'analogues' of metals, where lasers play the part of X-rays in analysis and dislocations and so on can be directly seen, rather than using inductive reasoning.

Several other points were also mentioned, such as some members of staff in Materials Departments also being members of Chemistry or Physics departments at the same time, in order to inject a sense of real materials into the courses of the latter. There was also a speaker who advocated the need for Ph.D.'s for students who have had industrial experience, and the University of Massachusets is paying special attention to this problem.

Friday, September 15th

A set of papers, rather out of the author's field, showed a great interest in polymers as fillers in other polymers and much concern for surface properties connected with such materials. There was much interest shown in surfaces, in connection with composites, at the Convention.

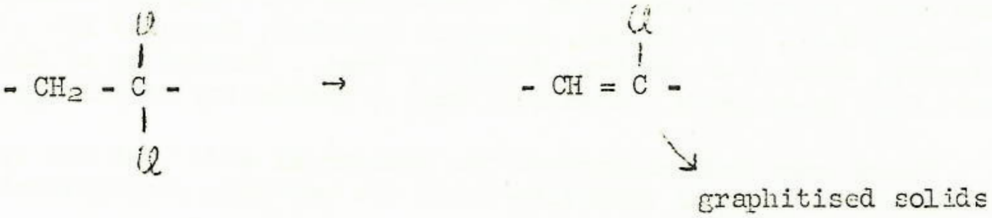
The second visit was to Daw Chemicals, Midland, Michigan. The general supervision of my stay there was by Dr. L.H. Lee.

Monday, September, 18th

Meeting with Dr. Wessling and Dr. Bohme

These gentlemen are working on the thermal degradation of poly vinylidine chloride and are having great trouble in getting repeatable results.

In simple terms the reaction is:-



$$-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}- \;\rightarrow\; -\mathrm{CH}=\overset{\mathrm{Cl}}{\mathrm{C}}- \searrow \text{graphitised solids}$$

The kinetics of dehydrochlorination are being examined, both from solid powders and from solutions, where solvent effects are also noted. A flow of nitrogen removes the hydrochleric acid gas which is absorbed in water and titrated. There is a good deal of evidence that crystal morphology and the formation of graphitic tar effects the kinetics of reaction and course of the degradation. Possibly initiation centres are at chain folds in the crystals. They and the writer were in agreement that a good deal of the published kinetics based on TGA is of no value whatsoever.

Meeting with Mr. C. Stacey

He is working on stabilises for Dow polymers, and is thus, most interested in the effect of oxygen and U.V. light. This involves measuring oxygen uptake of polymers by a sensitive menometric device. Induction periods are a measure of the effectiveness of the stabiliser. Stabilisers are complex alkyl phenols, or less probably thiophenols, i.e. they are conventional radical scavengers. Polymers being currently investigated are polystyrene, styrene/acrylonitrile copolymers and several types of rubber (natural, BRS, etc.).

Dr. Cobler, Mr. Wagner. Analytical Department Tour.

During this period I was shown their analytical section. This did not include N.M.R. or mass spectroscopy which is done in another section. The following are notes on pieces of apparatus:

1. Gel peneation techniques. An impressive commercial instrument was shown, having facilities for columns in series and being capable of handling 5-10 c.c. polymer solution. This plots out complete distribution curves and fractions may also be collected. The basic principle is, of course, a molecular sieve and the technique is complementary to column chromatography which depends on adsorption. The instrument is manufactured by Waters Associates, 61 Fountain St., Framingham, Mass.

2. Du Pont DTA apparatus, capable of collecting any materials given off by sample and a wide range of atmospheres etc. A differential scanning calorimeter was available and was regarded as less sensitive than DTA but obviously much more quantitative.

3. Commercial light scattering apparatus was available also an ultra centrifuge, where u.v. scanning of the tube measured the distribution of molecular weights. Vapour phase osmometry (which is rapid) was used for number average molecular weight.

4. Pyrolysis/Chromatograph was available on a home-made instrument; here small boats were placed in a coil furnace containing 5 mg of resin. Effluents were analysed by the usual KBr plug followed by infra-red, also by mass spectroscopy. The burner is mostly used for 'finger-print' work.

5. The thermo-gravimetric balance is an older glass-quartz spring type

(Jellineck); they did not appear familiar with the Stanton Thermal Balance and were interested to hear of it.

6. We discussed Attenuated Total Reflectance (ATR) for infra-red spectroscopes. The single reflection devices were found to give poor spectra, due to poor optical contact. This has been also the author's experience. For hard surfaces they have successfully used Multiple Internal Reflectance (MIR) which works well, several excellent MIR spectra of acrylonitrile were shown as a demonstration. This is important as surface degradation would be well investigated by MIR.

The author also delivered a lecture to their research department on 'Degradation of an Amine-cured Epoxide Resin between 210°C and 310°C'. Questions were lively and apparently the lecture was well received.

Tuesday, September 19th

Meeting Dr. Austin, Dr. Baney

These gentlemen are working on the pyrolytic degradation of silicone resins, but appeared much troubled by reproducibility of results; they spent time questioning me on our methods. It appears that in degradation of silicones a large number of cyclic products appear, due to favourable thermodynamics. This accords with the ease of synthesis of similar cyclic products as side reactions in resin manufacture.

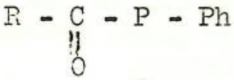
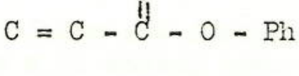
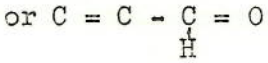
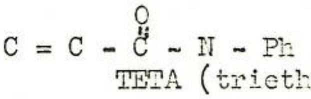
Meeting Mr. Bowen, Mr. Vranish, Dr. Minsker, Dr. Bursel, Dr. Meath, and Dr. Spradling.

Mr. Bowen described further work done by him on the degradation of epoxides, using films cast on sodium chloride windows, the degradation being followed by I.R. spectroscopy. (Similar to the methods of R.T. Conley(1)).

The first run was under oxidative conditions using a bis-phenol. A resin hardened by DDM p' diamino diphenyl methane, degradation occurring at 200°C.

All bands were weakened by the hydroxyl band more weakened relatively. (Film thickness was reduced).

The following bands were assigned:-

Ware No.	Structure
1750	 $R - \underset{\underset{O}{\|}}{C} - P - Ph$
1735	 $C = C - \overset{\overset{O}{\|}}{C} - O - Ph$
1718	R.CHO
1685	$C = C - COOH$
	 or $C = C - \underset{H}{C} = O$
1668	 $C = C - \overset{\overset{O}{\|}}{C} - N - Ph$ TETA (triethylene tetramine)

A similar resin, degraded likewise, but using triethylene tetramine hardener differed only in lacking the band at 1668 cm.$^{-1}$

Pyrolysis of a bis-phenol A resin hardened with TETA under oxidative conditions at 540°C yielded.

Bis-phenol A, allyl ether of isopropyl phenol, alkyl ether of isopropenyl phenol, isopropenyl phenol, isopropyl phenol C_2, phenols, cresols, 4 methyl cyclohexane, methyl pyrolle, phenol, toluene, benzene, cyclopentadiene, acetone, ethanol, carbon dioxide, propylene, methyl acetylene, methyl amine, ethane, ethylene, carbon monoxide, water, ammonia and methane.

Using DDM in the oxidate case certain other compounds were also observed, namely butyraldehyde, acetic acid, acrolein,methyl chloride, acetaldehyde, ethylene oxide, methanol and hydrocyanic acid.

With anhydride cure there is also a regeneration of the original hardener e.g. phthalic anhydride.

Mr. Bowen was in general agreement with the mechanisms put forward by us on epoxide degradation i.e. regarding dehydration and scission at the 'cure-link'.

Working lunch Dr. J. Lawrence Amos, Mr. Vranish, Dr. Lee, Mr. Bowen.

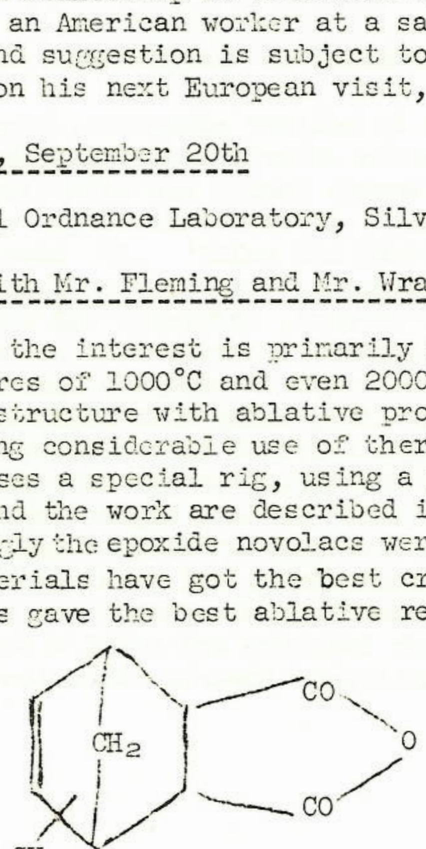
The writer outlined the broader activities of the College, and of the Materials Department to Dr. Amos who is Manager of Technical Liaison. They agreed a) to support the work by supplying C_{14} labelled products from their Texas centre at Freeport (where epoxides are produced) and b) to consider founding a Fellowship at Cranfield on epoxide degradation, if necessary supplying an American worker at a salary he would expect from Dow at home. This second suggestion is subject to inspection of the Department by Dr. Amos on his next European visit, in the spring of 1968.

Wednesday, September 20th

Naval Ordnance Laboratory, Silver Springs Maryland.

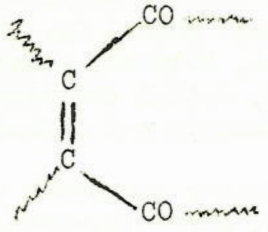
Meeting with Mr. Fleming and Mr. Wrasdilo

Here the interest is primarily in ablation and thus in degradation at temperatures of 1000°C and even 2000°C. Mr. Fleming attempts to correlate chemical structure with ablative properties, but also does general degradation work making considerable use of thermo-gravimetric analysis. For ablative work he uses a special rig, using a plug of silica flow filled expoxide, the rig and the work are described in reports (2) which he gave me. Interestingly the epoxide novolacs were regarded as the best resins, amine-cured materials have got the best cross-linking density, but in fact certain anhydrides gave the best ablative results, especially methyl nadic anhydride.



MNA

The crux of Mr. Fleming's work is this:- the anhydride hardeners with endo-methylene groups give much superior ablative materials to other hardeners. The ablated plugs in particular have superior physical properties, both mechanical and thermal conductivity. He explains this as due to a reverse Diels-Alder degradation reaction to yield structures such as



which may undergo cross-linking or graphitization in the For these reasons he recommends the replacement of phenolics by suitable epoxides in rockets, even though there is increased cost and some increased handling difficulty. Preliminary work on the ablative use of epoxides has already started.

Friday, September 22nd Seton Hall University, South Orange, N.J.
Professor R.Y. Corley

Though my visit had been finalised on August 8th, Professor Conley has become Chairman of Chemistry, Ohio State University, Columbus. In the move he had forgotten my visit and unhappily was in Columbus and could not be seen.

Conclusions

The following are general reflections on the American visit:-

a) There is considerable keenness in polymer education, especially towards graduate degrees. To me the education efforts seemed impressive, but industrialists complained that not enough people are being supplied and that the educational effort is too small. In the words of one speaker 'how many centries have we got to sit around and wall?' Dr. Amos at Dow, and several speakers at the Education Symposium were keen on polymer science, rather than artificial divisions of physics, chemistry and technology, especially as interesting work is often at a border-line between these fields. Graduate students do come forward in adequate numbers, but pure chemists and physicists do not, recruiting being from engineers, chemical engineers and metallurgists. The attitudes of pure chemists and physicists concern many educationalists, hence the desire to put more polymer science in undergraduate courses to act as 'bait' to take higher degrees. What we do in polymers at Cranfield fits in with many of their ideas, though the effort by their standards is on a small scale, and possibly we should give more thought to the practical and technological side of our work. The author has some experience of British industry and noted a very great difference in American Industrial attitudes towards educational matters in that they put pressure on the academics for higher degree men in polymer science in direct contrast to the situation in the U.K.

b) The work of Fleming at N.O.L. was particularly interesting, especially his view that epoxides make better ablate materials than phenolics. The epoxides in question are novolak and polyphenylene types and methyl nadic anhydride hardener and we should certainly, on that account, move over to the examination of these systems, more than amines. Possibly some work on ablation using a rig similar to Fleming's hardened systems may be also attempted, though he has a considerable lead in that aspect of the field.

c) The interest of Dr. Cohen of General Electric in the work on the electrical properties during degradation was strong, this contact will be followed up, they are also interested, for practical reasons in the chemical products of degradation.

d) In general, our views of epoxide degradation harmonise with those of American workers in the field. The radio-active work interests them and Dow propose to help with labelled compounds, also offers of resins and hardeners and so forth. It was stimulating to meet people such as Lee, Bowen and Fleming, who have made significant contributions to the field, which may grow in importance, both in electrical engineering (lower temperature degradation) and in ablation applications.

e) On the side of rheology and physics there is a great interest in polymeric fillers in polymers, e.g. rubber in polystyrene. Partly linked with this is a very considerable interest in surface properties.

Acknowledgements

The author would like to thank the College authorities and the Ministry of Technology for the means to make the visit and the American Chemical Society for their invitation to lecture to them. I would also like to thank Dow Chemicals and the U.S. Naval Ordnance Laboratory for their kind hospitality and help and also Professor A.E. Rheineck, North Dakota State University, Fargo for his help at the A.C.S. Meeting. Finally I would like to thank Dr. L.H. Lee, Dow Chemicals, for his hospitality and kindness at Midland, Michigan.

References

1. R.T. Conley and M.F. Dante — American Chemical Society. Div. of Organic Coatings and Plastics Chemistry. Chicago Meeting 24 No. 2, p. 135 (Sept. 1964).

2. G.J. Fleming — NOL TR 66-124
NOL TR 67-40