Summary of 1952 Elastomer Conference, Gordon Research Conferences[1]

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AN Elastomer Conference was held at Colby Junior College, New London, New Hampshire, June 30–July 4, as part of the 1952 Gordon Research Conferences sponsored by the AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. J. D. D'Ianni served as chairman, and M. Morton (Akron University) as vice-chairman. The program consisted of the presentation of a series of formal papers, followed by discussion led by selected participants. Fields covered were: emulsion polymerization, physical properties of latex, dynamic properties of rubber, crystallization phenomena and structural effects, chemistry of vulcanization, and degradation studies. Discussion leaders included W. V. Smith (U. S. Rubber), J. A. Davison (U. S. Rubber), H. L. Williams (Polymer Corporation), J. A. Yanko (B. F. Goodrich), J. Rehner, Jr. (Esso Laboratories), R. Buchdahl (Monsanto), A. W. Meyer (U. S. Rubber), A. M. Bueche (General Electric), D. Craig (B. F. Goodrich), C. M. Doede (Connecticut Hard Rubber), and J. O. Cole (Goodyear). The ensuing brief report of the significant results discussed at this conference is based largely on the exact wordage of summaries kindly supplied by each speaker.

Two papers were presented in the field of emulsion polymerization. E. J. Meehan (University of Minnesota) described new redox systems for the emulsion copolymerization of butadiene and styrene. One of the new systems makes use of the reaction between chromium (VI) and arsenic (III) in slightly alkaline (soap) medium to produce free radicals that initiate polymerization. This system is suitable for use at temperatures of 20°–40° C. Other new redox systems, developed for use at temperatures around 0° C, make use of the reaction between an iron (II) complex and an organic hydroperoxide to produce free radicals. The concentration of iron (II) in the system is maintained at a suitable value by the addition of a reducing agent, which continually reduces the iron (III) formed in the rapid reaction of iron (II) with the hydroperoxide. Hydrazine and sodium sulfide were found suitable reductants when ethylene diamine tetracetate was the complexing agent for iron. Studies on the mechanism of initiation of emulsion polymerization by persulfate were also reviewed and discussed.

M. Morton, in polymerization studies with chloroprene, found that the soap micelles are not the only important locus of formation of particles. Both the aqueous phase and the oil-water interface appear capable of initiating polymer particles, as evidenced by the marked effect of agitation on the polymerization rate. The presence of these additional loci of polymerization appears to be due to the exceptional reactivity of this monomer rather than to its solubility in water, which is relatively low.

In the symposium on the physical properties of latex, E. G. Cockbain (British Rubber Producers' Research Association) stated that the mechanism of the reversible aggregation of latex and synthetic emulsion particles depends on the nature of the adsorbed film stabilizer. If this is a soap or synthetic detergent, adsorption is no longer monomolecular when the soap concentration in the aqueous phase is appreciably greater than the critical micellar concentration. A secondary adsorbed layer of soap or detergent is believed to be formed, with the hydrocarbon chains oriented toward the aqueous phase, thereby rendering the surface of the disperse phase hydrophobic and causing aggregation. In systems stabilized by proteins, the pH and the ionic strength of the aqueous phase are the main factors controlling particle aggregation. In the presence of soaps or proteins and an additional hydrophilic colloid such as sodium alginate, secondary adsorption of the hydrophilic colloid probably occurs, leading to an interlinking of particles of the disperse phase.

The coalescence of latex or synthetic emulsion particles on heating in the presence of an organic heat-sensitizing agent such as polyvinylmethyl ether depends on both the interfacial activity and the negative temperature coefficient of solubility of the ether. Adsorption of the sensitizing agent on the rubber particles appears to be necessary for effective heat sensitization. To prevent the preferential adsorption of fatty acid soaps present in latex, the interfacial activity of the soaps may be reduced by a lowering of pH, addition of polyvalent cations, or similar means. Organic heat-sensitizing agents other than polyvinylmethyl ether were described, including the polyoxyethyleneoxypropylene diols. Suitable agents of this class show considerable promise as heat-sensitizing agents for natural latex.

The second paper on latex, by S. H. Maron (Case Institute of Technology), was a summary paper on

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[1] Work discussed herein by E. J. Meehan, M. Morton, S. H. Maron, T. W. DeWitt, R. M. Pierson, W. S. Richardson, H. E. Adams, and I. Auerbach was performed as part of research projects sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the government synthetic rubber program.

"Determination of Synthetic Latex Particle Size and its Distribution." The methods for particle size determination discussed were electron microscopy, soap titration, and light scattering, in which were included dissymmetry, wavelength exponent variation, and minimum intensity of scattering. Each method was considered from the standpoint of the experimental techniques involved and its advantages and limitations. Maron also gave a procedure by means of which it is possible to determine the particle size distribution of a latex from suitable differential creaming data.

The next topic for discussion was "Dynamic Properties—Effect of Molecular Weight and other Parameters." The first paper, entitled "Shear Dynamics in the Rubbery State," was presented by I. L. Hopkins (Bell Telephone Laboratories). T. W. DeWitt (Mellon Institute) summarized "Some Dynamic Studies on Fractions of Diene Polymers." A major objective of this program was the study of the relation between the structure and physical properties of synthetic elastomers. The response of the rubber to slow alternating stresses (0.0005–0.5 cps) was used as the basis of comparison. Insofar as possible, fractions of approximately the same molecular weight (200,000) were used in an effort to eliminate the effect of molecular weight and molecular weight distribution.

Four materials were surveyed for their behavior over a wide temperature range (−60° C to +100° C) and at several frequencies. Two polybutadienes, one prepared at 5° C and one at 50° C, and two butadiene-styrene copolymers, one with about 27 per cent styrene and one with about 15 per cent styrene, both prepared at 5° C, were thus studied. A very brief survey in the neighborhood of room temperature was also made of polybutadiene prepared at −20° C. The outstanding differences between these materials are found in the low temperature region. The temperature of maximum loss—and most rapid rise in modulus—is higher, the higher the styrene content. Crystallization, which occurs with the 5° C and −20° C polybutadiene, is accompanied by a decrease in the loss and an increase in the modulus—a relationship the reverse of that usually encountered.

Surprisingly enough, the three polybutadienes and two butadiene-styrene copolymers show little difference in their behavior at room temperature. For two of the polybutadienes fractions of different molecular weights were studied. Increased molecular weight leads to a decrease in loss and an increase in modulus. The effect of molecular weight appears to be at least as great as that of structural differences in the room temperature region. A comparison of these data with somewhat more complete data for high molecular weight polyisobutylene shows the somewhat unexpected result that, in the region of room temperature, this material has a much lower loss factor. A polyisobutylene of about the same molecular weight but an appreciably lower modulus is not strikingly different in loss factor from the diene polymers studied. Natural rubber was not studied, but data from the literature indicate that it is similar to high molecular weight polyisobutylene in its room temperature behavior.

R. M. Pierson (Goodyear) described some recent work correlating free-end fraction and resilience. Elastomer networks, the free-end fractions of which were varied over wide limits, were composed as to dynamic properties, particularly resilience. The free-end fraction, $\frac{2Mc}{Mn+Mc}$, was manipulated by varying either Mc, the molecular weight between cross-links, or Mn, the primary number average molecular weight. Dynamic resilience properties of each of the elastomers studied—principally "cold" GR-S and natural rubber—dropped markedly as the free-end fraction was increased above 10–15%. Since practical processing techniques require operation within rather narrow limits of the weight average molecular weight, Mw, the desirability of utilizing polymers of low ratios of Mw/Mn (narrow distribution) for maximum resilience properties was brought out.

The first paper in the section on crystallization phenomena and structural effects was by W. B. Reynolds (Phillips Petroleum) on "Hydrogenated Polymers." Hydrogenation of synthetic elastomers, such as polybutadiene and copolymers of butadiene with various vinyl compounds, produces a group of thermoplastic resins possessing interesting properties. These materials resemble polyethylene but are generally more flexible, particularly at very low temperatures. For example, hydrogenated polybutadiene can be struck sharply at −100° F without shattering, and is not brittle (even though extremely hard) at liquid nitrogen temperatures.

Hydrogenation can be carried to various stages, depending upon the properties desired. For most plastic applications an unsaturation of 5–30 per cent of the original is desirable. Higher unsaturations increase the ability of the products to undergo vulcanization. Some of the more important potential applications for hydrogenated polymers are in wire and cable coating, films, tubing, and various molded items. These hydrogenated high polymers are now in the development stage in a program that has been supported in part by the Office of the Quartermaster General.

W. S. Richardson (Mellon Institute) summarized "The Influence of Polymerization Conditions on the Structure of Diene Polymers," reviewing the microstructure of polyisoprenes and polybutadienes prepared in bulk and emulsion systems between −20° and 100° C. The general features of the structure of alkali metal and alfin polymers were also briefly mentioned. New work was reported on three groups of polymers: polymers prepared in bulk between room temperature and about 300° C, polymers prepared at room temperature in bulk under high hydrostatic pressures, and polymers prepared between −80° C and +40° C in solution using Friedel-Crafts catalysts.

The resulting polymer structures as obtained from infrared spectra show that, as the preparation temperature is raised, the polybutadienes tend toward roughly equal *cis*- and *trans*-concentrations (40 per cent), the 1,2 addition concentration remaining about 20 per cent, as it is in lower temperature preparations. In the case of the polyisoprenes, the *cis*- 1,4 addition increases only up to 100°–125° C and then decreases gradually for higher temperatures. The 3,4 addition remains sensibly constant over the whole temperature range, but the 1,2 addition decreases at higher temperatures, being almost absent at 300° C. It is not known whether this means the 1,2 addition is not formed at higher temperatures or whether it is formed and subsequently used up in some side reaction.

Polyisoprenes and polybutadienes were prepared at about 5000, 8000, and 10,000 atmospheres. As far as structure is concerned, there appears to be little variation over this rather limited pressure range. The polyisoprenes are roughly comparable to atmospheric pressure polymers prepared at lower temperatures (−20° C). This does not seem to be true of the polybutadienes, which are more nearly comparable to slightly higher-temperature, atmospheric-pressure polymers as far as 1,2 and *trans*- 1,4 additions are concerned. Since we do not analyze for *cis*- 1,4 addition in the polybutadienes, it is not clear whether the remainder of these polymers is composed of *cis*- 1,4 addition or whether there are other types of structures (cyclics, etc.) present.

Cationic polymers of polybutadiene and polyisoprene were prepared at room temperatures, −30° C, and −80° C, in solution using various Friedel-Crafts catalysts (BF_3, $SnCl_4$, and $AlCl_3$). Although some linear addition is present in these polymers, they show generally a lack of unsaturation varying between 20 and 80 per cent. Within the linear polymer present, the distribution among external and internal types of additions appears to be similar to the free radical-type polymers. Two other papers in this section were presented by F. M. Rugg (Bakelite Division, UCC), on "Infrared Structural Studies of Polyethylene and Changes on Oxidation," and by M. L. Dannis (B. F. Goodrich), on "Plasticizers for Polyvinyl Chloride."

Three papers were included in a comprehensive and lively discussion of the "Chemistry of Vulcanization." B. C. Barton (U. S. Rubber) discussed "Mechanism of Sulfur Vulcanization of Rubber." In the accelerated reaction of sulfur with rubber, the yield of cross-links is dependent on the time and temperature of vulcanization and on the concentration of sulfur, accelerator, zinc oxide, and fatty acid. When the conditions necessary for the maximum yield of cross-links per unit of combined sulfur are met, a linear relationship exists between the number of cross-links and both combined sulfur and zinc sulfide formed in the vulcanization reaction.

Calculations based on the Wall equation relating equilibrium modulus to number of cross-links suggest that, when the conditions for a maximum yield of cross-links are met, one molecule of zinc sulfide is produced for each cross-link formed. The reactivity of various alkyl and alkylene and mono- and disulfides with natural rubber indicates that two types of reversion occur in natural rubber vulcanizates. The most common type occurs rapidly at normal curing temperatures and is due to rupture of alkylene disulfide cross-links.

H. E. Adams (Firestone) reported that the cross-linking of natural rubber vulcanizates, prepared by Captax accelerated sulfur cures, is directly proportional to the amount of soluble zinc present at a constant sulfur level. One cross-link is formed for each zinc atom added and every two sulfur atoms that combine with the rubber. Zinc sulfide is produced in the degradation reaction that destroys the cross-linking. I. Auerbach (Goodyear) discussed the mechanism by which mercaptobenzothiazole (MBT) accelerates vulcanization. Its course in the vulcanization process was followed by tagging it with radioactive sulfur. It was found that the zinc mercaptide of MBT is the initial product and that this compound reacts with sulfur in the presence of rubber to remove a hydrogen from the rubber and regenerate MBT. The rubber in this active form reacts with sulfur to produce a cross-linked polymer.

Discussion of "Degradation Studies" was initiated by R. Simha (New York University) with a detailed examination of the "Free Radical Mechanism of Degradation," followed by E. G. Cockbain's report of W. F. Watson's work on "The Cold Mastication of Rubber." The degradation whereby rubber is plasticized by cold-milling depends on an initial rupture of the rubber hydrocarbon into polymeric free radicals by the applied shearing forces. These free radicals recombine under nitrogen, a fact that explains the long-known observation of no plasticizing in an inert atmosphere. Oxygen readily attacks these free radicals and changes the eventual termination into a reaction not involving combination of polymeric radicals. The anomalous negative temperature coefficient of plasticization by cold-milling is explicable by the increasing viscosity and, hence, applied shear. The mechanism is critically tested by milling in nitrogen after addition of compounds likely to function, as does oxygen, by interfering with the secondary recombination after the primary mechanical scission. Forty-seven substances are listed as competing with recombination with varying efficiency, from mercaptans as effective as oxygen to substances, such as phenol, with only a detectable action. A similar mechanism applies to the cold-milling of synthetic rubbers. With certain substances, such as maleic anhydride and chloranil, the eventual radical termination involves the rubber molecules, giving branched or cross-linked rubbers.

The probable allylic structure of the radicals formed by rupture and their chemical activity toward the added compounds were discussed. The factors influencing efficient mastication, the function of peptizers, and degradation under other types of rapid deformation were considered according to the mechanical-rupture mechanism.

The program was concluded by a study of the "Oxidation of Neoprene," as reported by E. K. Gladding (Du Pont), who stated that oxidation of poly-2-chlorobutadiene (neoprene) and poly-2,3-dichlorobutadiene is accompanied by the formation of peroxidic materials, carbonyl compounds, acids, and acid chlorides. The acid chloride function is a characteristic oxidation product of these chlorine-substituted polymers, and experiments with model compounds show that it is formed from a configuration equivalent to two adjacent monomer units of the polymer. The colored products that form during neoprene oxidation are believed to consist of structures that can arise through polymerization (followed by elimination of HCl), of β-chloro-α, β-unsaturated carbonyl, or carboxylic acid intermediates formed by oxidation.

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A Discussion of Photosynthesis

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ASPECTS OF PHOTOSYNTHESIS from the initial absorption of light to the ultimate syntheses were scrutinized by some 80 research workers of many scientific disciplines at Gatlinburg, Tennessee, October 29–November 1, 1952.[1] The free discussion that was encouraged at this meeting yielded many clues for further study of the photosynthetic process.

Light utilized in photosynthesis is absorbed by the several chlorophylls and bacteriochlorophylls, and by open chain tetraphyrolles and carotenoids of various organisms. The absorbed energy is transferred between molecules of these pigments, as determined by the molecular structures and permitted by the organization of the pigments in the grana. The energy is used to effect the chemical transfer of hydrogen from some molecule, such as water, to unidentified primary acceptors. The acceptors then transfer hydrogen to compounds formed during carbon dioxide fixation, probably both by known and still unknown enzymatic systems.

Energy level systems for porphins and tetrahydroporphins were considered as a basis for discussion of the spectroscopic properties of related, but less symmetrical, chlorophylls that are effective in photosynthesis (J. R. Platt, University of Chicago). Such molecules have a triplet level of energy lower than the first excited singlet level that gives rise to fluorescence emission. This triplet level, having a long life of the order of 10^{-4} seconds, is responsible for photochemical reactions. The separation between those two levels determines how much of the energy of the absorbed light is degraded and, therefore, is not available for chemical activation in photosynthesis. Unfortunately, no direct calculation of this separation is available. Estimates, based on the measured values for the levels of several other compounds, however, indicate that the quantity might be as small as 5–10 kcal. for chlorophyll (M. Kasha, Florida State University; Platt).

Another singlet level may lie very close to the fluorescent level, but transitions between the former and the ground level are not observed, since they would be of the forbidden N-II type. If such a level lies between the fluorescent singlet level and the lowest triplet level, radiationless transitions between the two would be facilitated and fluorescence weakened.

Attention next turned to some reversible photochemical changes of chlorophyll, which are probably related to the primary acts of photochemical reactions sensitized by chlorophyll *in vitro* and possibly of photosynthesis. It is known that the red absorption of oxygen-free solutions of chlorophyll in methanol is reduced when such solutions are illuminated with intense, visible light. When the light is extinguished, the solution very quickly returns to its original color.

Experiments were described in which chlorophyll was dissolved in a rigid solvent, at liquid-nitrogen temperatures (H. Linschitz, Syracuse University). Under these circumstances the color change was much more marked, but the time required for the dark reversal of the photochemical process was too short to measure. If certain quinones were added, the photoproduct was stable so long as the solvent remained rigid. If the solution was warmed, the original color of the chlorophyll returned instantly when the solvent glass melted. The absorption of the labile photoproduct of chlorophyll was much less than that of normal chlorophyll in the red and blue but had a marked maximum in the green. This photochemical reaction is possibly an oxidation of the chlorophyll

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[1] The conference was supported by the National Science Foundation, the Office of Naval Research, and the Atomic Energy Commission. This report combines summaries for individual sessions, which were prepared by R. S. Livingston (University of Minnesota), E. Rabinowitch (University of Illinois), C. S. French (Carnegie Institution of Washington), F. Daniels (University of Wisconsin), B. Kok (Wageningen University), and M. Kamen (Washington University), who served as chairmen. Discussions were introduced by J. R. Platt (University of Chicago), E. C. Wassink (Wageningen University), R. Hill (University of Cambridge), M. Calvin (University of California, Berkeley), F. S. Brackett (National Institutes of Health), and H. Gaffron (University of Chicago).