Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Recent Developments in Solid-Propellant Binders

H. E. Marsh JR.[a]
[a] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

To cite this Article Marsh JR., H. E.(1969) 'Recent Developments in Solid-Propellant Binders', Journal of Macromolecular Science, Part A, 3: 7, 1397 — 1418

To link to this Article: DOI: 10.1080/10601326908051834

URL: http://dx.doi.org/10.1080/10601326908051834

J. MACROMOL. SCI.–CHEM., A3(7), pp. 1397-1418, November, 1969

Recent Developments in Solid-Propellant Binders

H. E. MARSH, JR.

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

SUMMARY

The complex and important role of the propellant binder in solid-propellant rockets is described. The severe weight problems of space exploratrion cause high propellant performance to be of major concern in a highly competitive field. Binders contribute to performance, not only in terms of fuel value, but by being compatible with energetic components and by providing good mechanical properties. Both sterilization required for planetary landings and compatibility problems of new energetic oxidizers generate new requirements too stringent for existing binders; only binders composed essentially of saturated aliphatic hydrocarbon are predicted to be suitable. Several saturated-binder developments are in progress. The achievements of one of these programs, based on free-radical synthesis, are evaluated against the goals of the new binder.

INTRODUCTION

New approaches to polymer synthesis are maturing at just about the right time to fulfill the needs of space exploration for improved solid-propellant binders.

---

†This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

A few years ago, the decision was made that the surest way to avoid carrying earth organisms to the surface of Mars would be to apply dry heat to hermetically sealed landing vehicles. This decision led to the requirement that any proposed propulsion systems should survive six 53-hr cycles at 275°F for proof testing.

Increased specific impulse continues to be a major goal for space rockets, especially for upper stages, retro motors, and so forth. One of the general avenues explored in recent years to increase available solid-propellant specific impulse has been an attempt to harness several oxidizers with greater energy than ammonium perchlorate. Of chief interest are nitronium perchlorate hydrazinium diperchlorate and hydroxylammonium perchlorate.

Established propellant binders based on polydienes and polyethers are not suitable for either application. Incompatibilities ranging from extensive postcuring to explosion were encountered with the new oxidizers. Although the binder materials are reasonably stable alone at elevated temperatures encountered in sterilization, they are not stable in the presence of ammonium perchlorate.

It became readily apparent that the new binders required to satisfy these needs must be saturated in order to work at all, and it had to be determined whether or not these goals could be reached, even with improved binders. It is reasonable at this time to say that most of the objectives will be met. Saturated binders have been developed and improved ones are being developed. Considerable progress has been shown in solving the sterilization and oxidizer compatibility problems by using these new materials.

A general discussion of the whole field of saturated binders is beyond the scope of this paper. This paper concentrates on the work of the Jet Propulsion Laboratory (JPL) and the Union Carbide Corporation* in this field, in connection with the overall requirements for a high-performance space propellant.

ROLE OF THE BINDER IN SOLID-PROPELLANT MOTORS

The development of specific improved characteristics in a new product, such as a propellant binder, is of little use if it is achieved by sacrificing some other important quality. This is especially true with any component

---

*Principal JPL investigators are the author and Dr. J. Hutchison (now at Heidelberg on a postdoctoral program). Union Carbide Corporation's investigators, working under JPL Contract 951210, are Dr. J. E. Potts and Dr. A. C. Ashcraft, Jr.

Table 1. Space Mission Requirements for Solid-Propellant Motors

I. General
  A. Availability
  B. Safety
  C. Reliability
  D. Economy
II. Function
  A. Performance
  B. Thrust-time program
  C. Controllability
  D. Accuracy
III. Compatibility
  A. Fit with spacecraft configuration
  B. Capability of withstanding expected environments
  C. Minimum need for special treatment or handling
  D. Minimum deleterious effect or restriction on the mission

of an integrated system for space exploration because of the many competing requirements. Table 1 lists the requirements for a space rocket motor. This list will serve for binders as well, because a binder is not really developed until it is used in a propellant that can be a part of a motor suitable for some mission. For economic reasons, a propellant with universal applications would be more suitable (item I-D, Table 1). With the saturated binders, although an attempt is made to provide chemical ruggedness for higher performance (item II-A, Table 1) and better environmental capability (item III-B, Table 1), availability (item I-A, Table 1) is the important factor.

It is important to explain briefly the role of the binder in a high-performance motor in order to identify the key requirements for binders. Mainly, these requirements revolve about performance and reliability over a fairly wide range of temperatures.

Velocity and payload mass together define rocket motor performance output (high velocity and/or higher mass represent high performance). Specific impulse and propellant mass fraction (propellant mass as a fraction of total motor mass) are the properties of a motor that produces this performance. In Fig. 1, which is applicable to many upper-stage and spacecraft propulsion requirements, it is shown that the characteristics of a new propellant affecting mass fraction must be up to standards if the advantages of a higher specific impulse are to be realized. A loss of 1% in mass fraction is equivalent to a loss of between 1 and 2% in specific impulse.

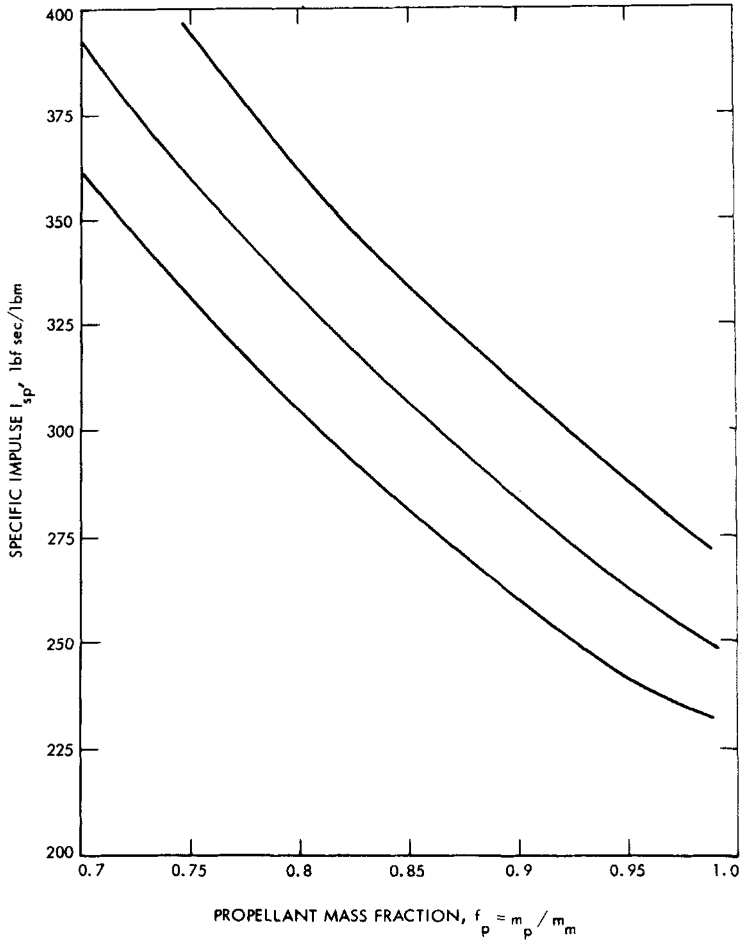

Fig. 1. Motor performance trade-off.

Binders contribute to motor performance in three ways: fuel value, compatibility with energetic oxidizers, and mechanical properties. The last-mentioned contribution is usually the most important. Propellant mass fraction, previously mentioned as a key factor in performance, depends more on propellant mechanical properties than on any other variable. This is easily visualized in Fig. 2, which shows the design of a typical high-performance space motor.

Figure 2 is a diagram of the Advanced Technology Satellite motor, a

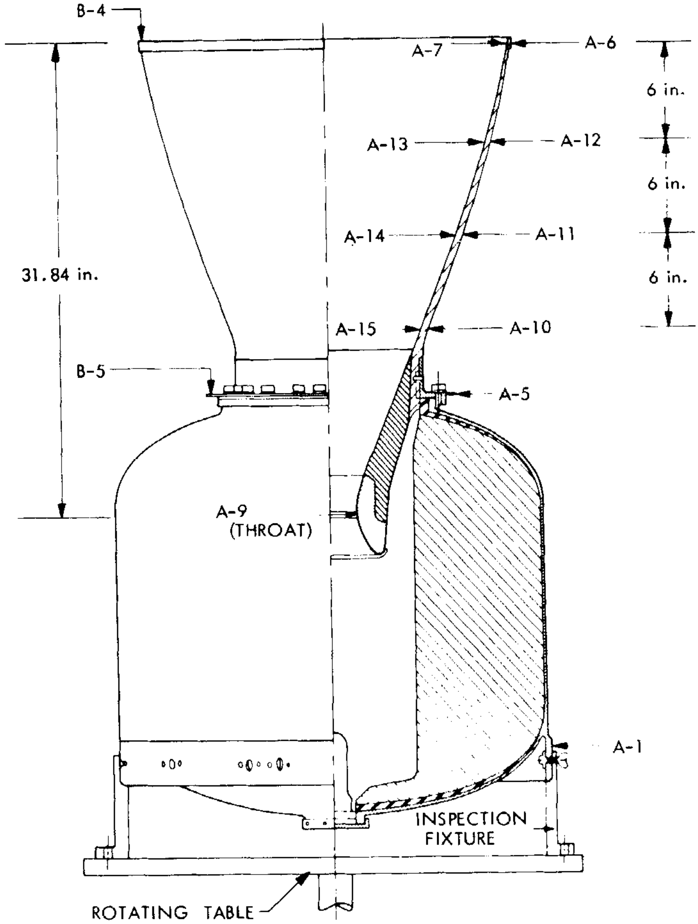

Fig. 2. ATS motor assembly.

JPL product used as the kick stage for synchronous satellites. The mass distribution of this 840-lb motor is 2.8% for the chamber, 4.5% for the nozzle, 1.6% for the liner (an inert rubber compound for insulating the chamber), 0.7% for the igniter (including safe-and-arm device), and more than 90% for the solid propellant. Such a structural assembly is reliably capable of withstanding the various forces and strains of temperature cycling, rapid pressurization, acceleration, vibration, and storage in any orientation because of the good rubbery properties of the propellant. This propellant is composed of aluminum, ammonium perchlorate, and a polyether/urethane binder. The binder, which provides the elastomeric properties, is 20% of the propellant mass; some propellants have as little as 12% binder.

If the typical modern solid propellant were not made from a good rubber, it would not be possible to integrate it into the chamber in the manner represented in Fig. 2. It should be noted that the propellant is bonded, through the liner, to the chamber wall throughout the entire interface. Severe mechanical forces and strains are imposed on case-bonded propellants by environmental factors. Case-bonding was first developed at JPL in the mid-1940s [1], with polysulfide rubbers. Since solid propellants burn only on exposed surfaces, case-bonded grains are designed to burn from an inner surface outward, and the cylindrical portion of the chamber wall is protected from the flame until burn-out. The tapered insulation thickness is necessary to protect those chamber surfaces exposed earlier. Another important feature of the polysulfides, and their descendants, is their castability in the uncured state as highly filled viscous slurries.

In summary it can be said that, whatever else a new solid-propellant binder contributes, in order to be competitive in propulsive performance it must also form castable slurries of appropriate composition that will cure to a material with good rubbery properties over required ranges of temperature.

GOALS FOR SATURATED BINDERS

As a consequence of the critical role of the propellant binder, the general goals for the saturated-hydrocarbon binder program fall into two categories. Prepolymers must be developed that, besides being chemically rugged, will have microstructure yielding good processing and elastomer properties. A good curing system is necessary, both for processing and to form a good rubber network structure. These points are illustrated in Fig. 3.

The detailed goals of the JPL program for prepolymers are shown in Fig. 4. First, the binder should be saturated. An obvious way to make a saturated-hydrocarbon, functionally terminated prepolymer is to hydrogenate one of the commercially available carboxyl-terminated polybutadienes (CTPB). This was tried by JPL scientists and several others. The problem was that the product was a wax demonstrating a high degree of crystallinity due to the preponderance of linearity in the aliphatic chains. Nevertheless, the materials were compatible with high-energy oxidizers. Both anionic and free-radical polymerization syntheses have since been developed to produce sufficient pendent side chains to eliminate this characteristic. The main

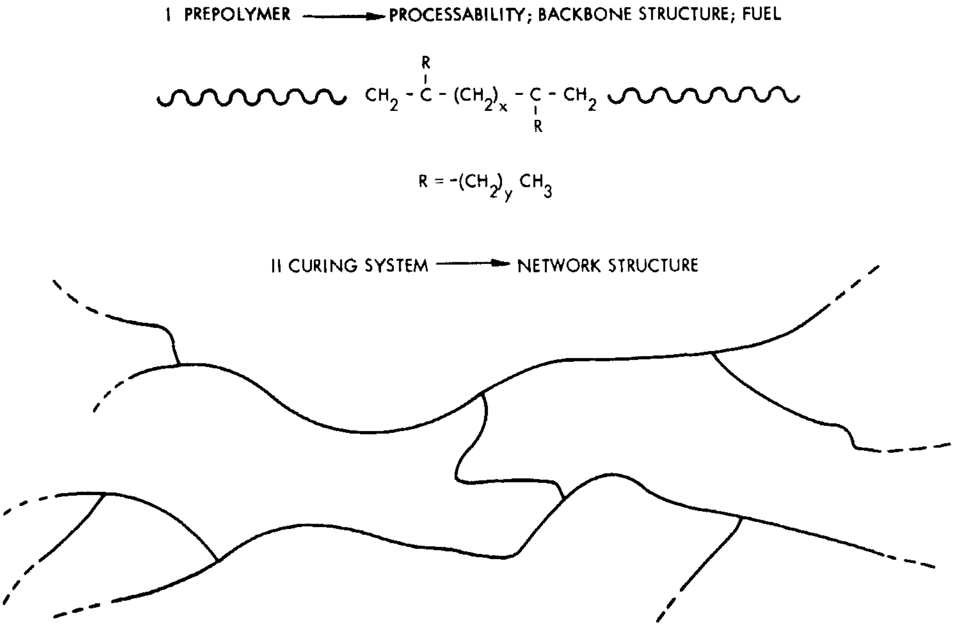

Fig. 3. Binder general goals.

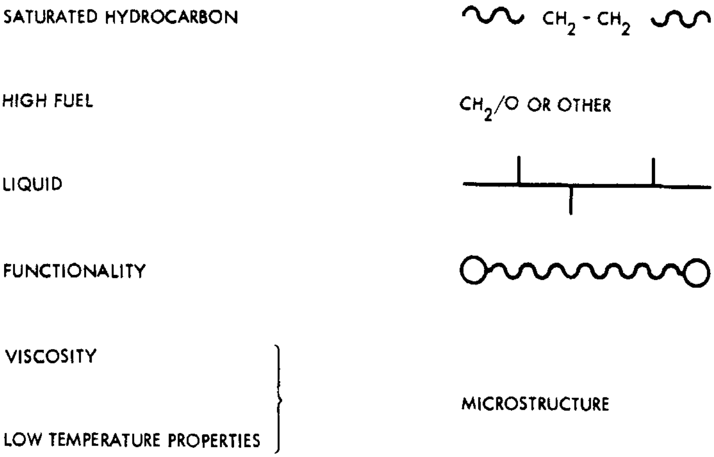

Fig. 4. Prepolymer goals.

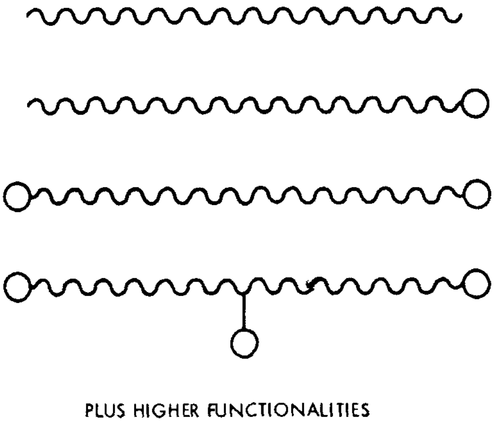

Fig. 5. Typical prepolymer, functionality distribution.

value attained from the attempts at hydrogenating existing diene prepolymers was the demonstration of survival of the carboxyls in this step.

High molecular weight, not listed in Fig. 4, is implied in the goals for high fuel value and good low-temperature properties. As far as the new synthetic methods are concerned, molecular weight is limited by the difficulty in attaining high functionality and the need for viscosities low enough to permit processing.

Good functionality is a goal for prepolymers only because it is a requirement for curing to form good rubber networks. The attainment of a high fraction of linear chains terminated functionally on each end has been one of the big problems with the new syntheses. A mixture (Fig. 5) of mono-, di-, and trifunctional material plus, in some cases, a fraction of product with no functional groups at all, is obtained rather than the desired difunctional product.* The anionic and free-radical syntheses theoretically involve the sequential steps of initiation, propagation, and termination. With the free-radical process, functionality problems can occur from nonideal reactions during any one of these steps. Since some of the anionic polymers start in the middle and grow in both directions, initiation is less likely to be troublesome. Analysis for functionality is an important matter.

---

*Molecular-weight distribution, also present, is not covered in this paper.

Table 2. Potential Saturated Prepolymers

Company	Saturated prepolymers
Union Carbide	Ethylene/neohexene
Union Carbide	Ethylene/C_nH_{2n}
Thiokol	Butadiene/diene; hydrogenated
Thiokol	HC polymer; hydrogenated
Thiokol and Jet Propulsion Laboratory	Low-oxygen polyester
Jet Propulsion Laboratory	Polyisobutylene
Rocketdyne	Polybutadiene star
United Technology Center	Polyisobutylene
General Tire and Rubber	Polybutadiene

It is even more desirable to determine functionality distribution. One approach was covered in the symposium* by Muenker; another approach is being studied at JPL [2, 3].

Table 2 lists the known major efforts at synthesizing saturated-hydrocarbon prepolymers. The Thiokol polydiene, the Rocketdyne star, and the General Tire and Rubber polydiene are anionic. The latter, known as Telagen, is available commercially in pilot plant quantities. At the symposium, Dr. DiMilo of Aerojet-General Corporation, a subsidiary of the General Tire and Rubber Co., discussed some studies with Telagen. Current JPL sterilizable propellant progress is based on the Telagen polymer [4].

The JPL approach to polyisobutylene (PIB) is cationic; UTC's PIB is made by oxidative scission of high polymers. The Thiokol/JPL prepolymer is a low-oxygen polyester that has as its major ingredient dimer acid (Emery Industries, Inc.), yielding a product with up to 36 carbon atoms between ester links (not all in a single chain, however).

---

*Symposium on Polymers in Space Research, Von Karman Auditorium, Jet Propulsion Laboratory, Pasadena, Calif., July 15-17, 1968, cosponsored by the Polymer Group of the Southern California Section of American Chemical Society and JPL.

UNION CARBIDE PREPOLYMER DEVELOPMENT–THE FUNCTIONALITY PROBLEM

The remainder of the discussion about prepolymer synthesis is devoted to Union Carbide's work with copolymers of ethylene. Union Carbide's early work was based on two special features–copolymerization of ethylene and neohexene, and the use of a high concentration of initiator–in an otherwise conventional batchwise, high-pressure, free-radical polymerization in solution (Fig. 6). Neohexene will not homopolymerize but will copolymerize with ethylene, and furthermore, company researchers reasoned that neohexene was the only alpha-olefin that could not hydrogen-transfer. The extra initiator was used to keep the molecular weight low, and these researchers counted on mutual recombination of growing free radicals to be the major mode of termination [5].

The results of early polymerizations, in which azo-bis-isobutyronitrile (AIBN) was used as initiator, supported these theories. It was found that

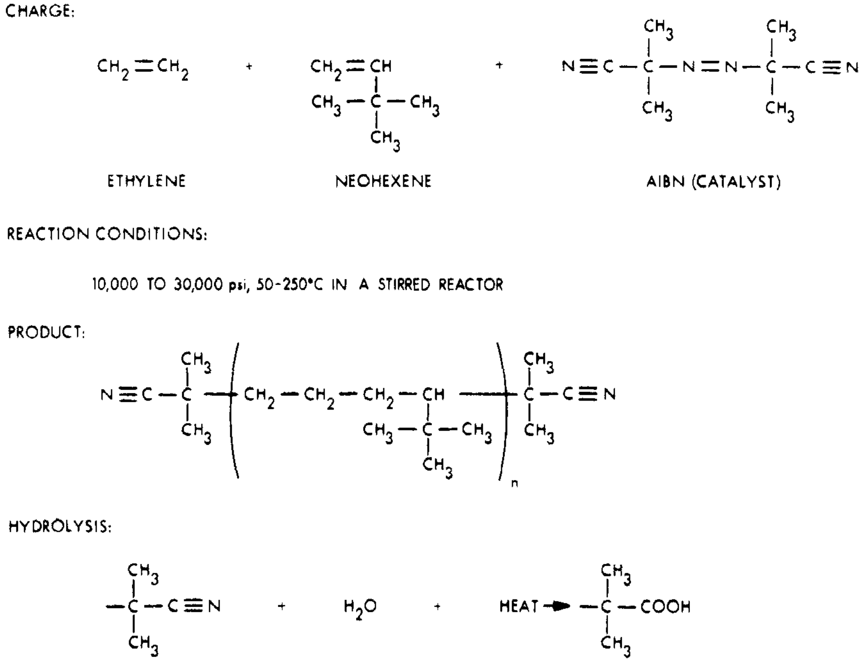

Fig. 6. Union Carbide prepolymer synthesis.

the proportions of the two olefins could be regulated so as to produce prepolymers ranging from wax, through paste, to viscous liquid [5].

First measurements of functionality based on vapor pressure osmometry (VPO) molecular weights and total nitrogen of the preliminary product indicated that the expected difunctionality had been attained. However, after hydrolysis, the functionalities dropped to about half–averaging one carboxyl per molecule. The cause of this undesirable result was not easy to find. Ultimately, it was discovered that the initiating radical resulting from the decomposition of AIBN underwent a rearrangement and that the initiating free-radical species actually consisted of an equilibrium mixture of two isomeric forms: the desired isobutyronitrile and a ketene imine structure. There was no way of converting the end group arising from the latter to the desired carboxyl group [5].

Following this discovery, many other initiators were tried. Peroxides were avoided because appropriate ones were not soluble to the required concentrations in the system, leading to possible hazard in the pumps.

A type of initiator that initially showed promise (Fig. 7) was a group of ester counterparts of AIBN; the one illustrated is dimethyl-α,α′-azobisisobutyrate [6, 7]. However, functionalities again were low, and, in addition,

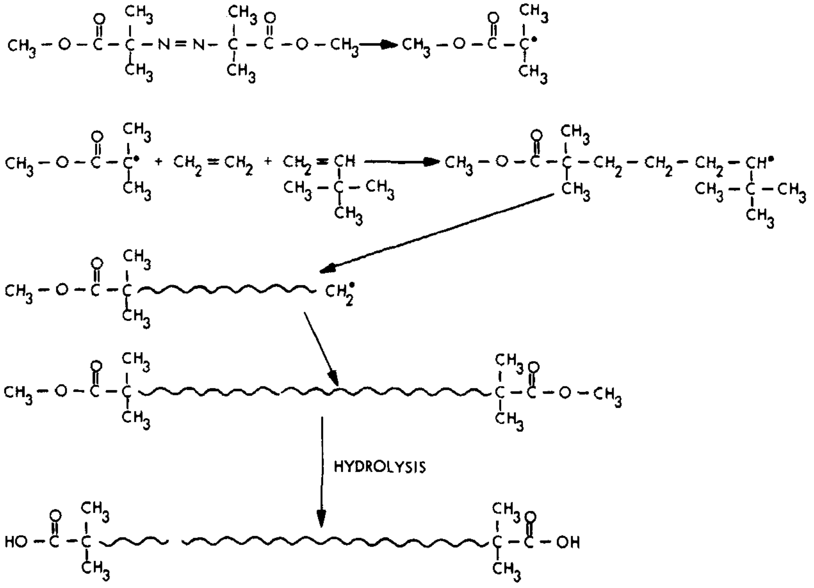

Fig. 7. Free-radical polymerization.

an insoluble polymer phase was observed. It was determined that the ester radicals disproportionated to form methyl isobutyrate (MIB) and methyl methacrylate [8]. A homopolymer of the latter product was the insoluble polymer previously mentioned, which by itself would not have been detrimental. However, the former (MIB) was a strong hydrogen-transfer agent, because of a tertiary hydrogen, and chains terminated by this step would have no functional group. Chain transfer was one of the major problems anticipated in this synthesis, and every attempt was made to avoid it. Failure to accomplish this led Potts and Ashcraft of Union Carbide to attempt to make use of chain transfer. These researchers reasoned that, perhaps, telomers could be converted to the desired difunctional prepolymer chain molecules [9].

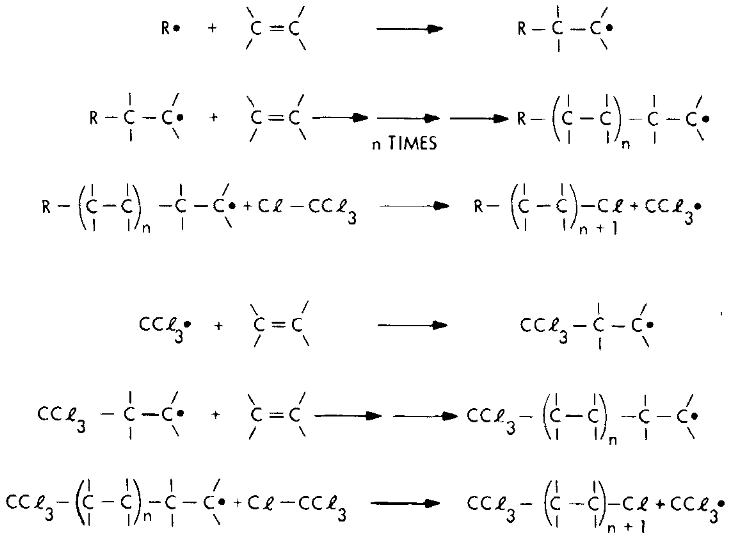

Fig. 8. Functionality attained through telomerization.

Potts and Ashcraft decided to put this idea to the test. They used carbon tetrachloride, a good chain-transfer agent, and achieved apparent functionalities close to 2, with the reaction following the scheme shown in Fig. 8 (in other words, analysis showed nearly four chlorine atoms per molecule, represented in the last line of Fig. 8). This showed that the technique would indeed be successful. In the main, reaction conditions were the same. The major difference was a drastic reduction in the

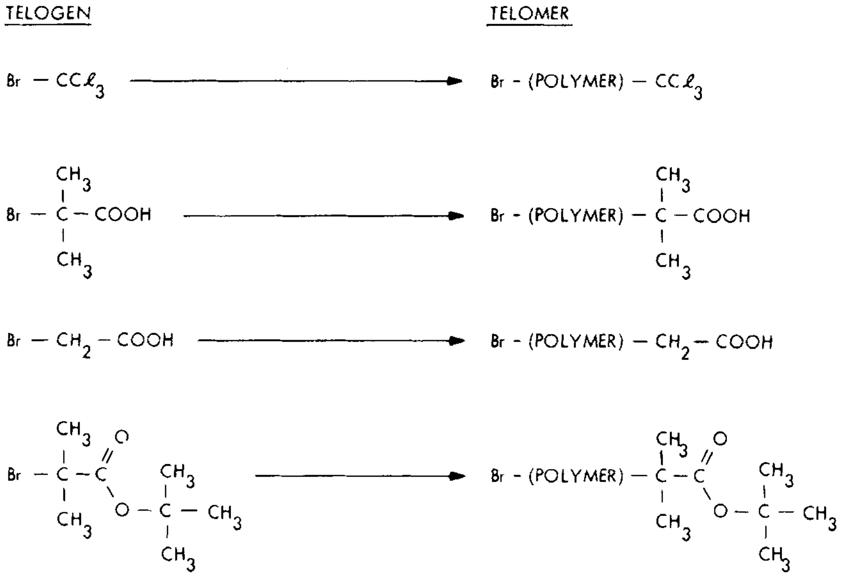

Fig. 9. Chain-transfer agents.

concentration of azo initiator (just enough to initiate the reaction) and a dependence on the chain-transfer agent for the bulk of initiation and control of molecular weight.

Actually, carbon tetrachloride is not a good transfer agent for a practical system, because there is no good method to convert its trichloro end group to a carboxyl. Therefore, Potts and Ashcraft looked into the use of other agents, such as those illustrated in Fig. 9 [10].

The last agent in Fig. 9, and also a corresponding methyl ester, were found to be very effective. The bromo end group is converted by dehydrobromination to an olefin followed by oxidation [11]. The functionality of the polymers thus produced is illustrated in Table 3, which shows data from early telomer runs [12]. These results demonstrate a great improvement in functionality, if it is recalled that the other methods had led to essentially monofunctional products. Moreover, quantitative conversion of the bromo groups has also been achieved. These results have all been obtained in a batch reaction process. More recently, a continuous stirred reactor was adapted for use in this synthesis. In this mode of operation, the beginning and ending transient products can be separated from the main product, with resulting improved functionality and higher molecular weights.

Table 3. Functionality of Telomer Samples (Union Carbide data)

Run	Molecular weight, M_n	Br/molecule	COOH/molecule	Total functionality
38	415	0.906	0.808	1.71
39	417	0.897	0.861	1.76
40	425	1.073	0.856	1.93
41	420	0.909	0.844	1.75
42	452	0.942	0.896	1.84
43	457	0.907	0.892	1.80
44	432	0.896	0.876	1.77
45	456	0.917	0.878	1.80
46	450	0.893	0.943	1.84
47	456	0.897	0.882	1.78

PREPOLYMER MICROSTRUCTURE AND FLOW PROPERTIES

All saturated-hydrocarbon prepolymers that we have looked at so far, except polyesters of dimer acid, are more viscous than they should be for effective propellant processing. As expected, hydrogen-bonding of carboxyls aggravates the problem. Since two of the goals mentioned in Fig. 4 indicate the desirability of higher molecular weights, the strong positive relation between molecular weight and bulk viscosity is a further obstacle to the employment of saturated binders.

The same effect is seen with regard to glass transition temperatures, T_g. None of the saturated-hydrocarbon prepolymers appears to have T_g lower than -55°C. The T_g measured on a prepolymer of 1000-5000 molecular weight is not a direct measure of that property in propellants made from it. However, if the prepolymer has poor low-temperature properties, the propellant is not likely to be better in this respect.

As an illustration of the criticality of microstructure, a small study was made to determine the effect of varying extents of hydrogenation of a polybutadiene prepolymer on T_g [13]. The results shown in Fig. 10 make it clear that a saturated chain is considerably stiffer than its unsaturated counterpart. In the figure, it should be noted that the quantity plotted in the abscissa is a softening temperature measured in a penetrometer test. This is probably as good a measure of T_g as a tan δ peak temperature in a torsion pendulum experiment. No crystallization effect is thought to be present here. The

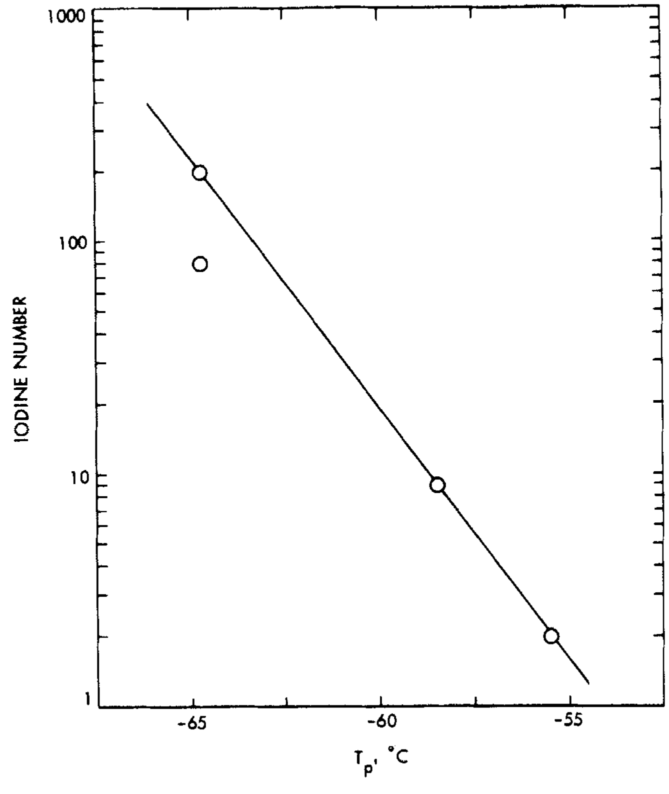

Fig. 10. Effect of unsaturation on glass transition temperature.

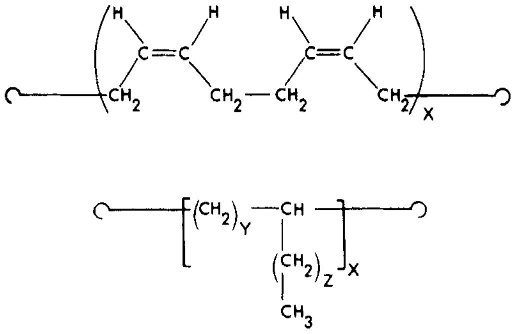

Fig. 11. Viscosity and Tg, backbone microstructure.

material was one of the telagens (GTR), which is a polybutadiene with enough 1,2 structure to make it amorphous. Several samples were hydrogenated to varying extents and characterized.

Considering the 1,4-polymerized butadiened shown in Fig. 11, the nonrotation about the double bonds in cis-polybutadiene is apparently more than compensated for by less than normal restricting environment for the adjacent single bonds. This advantage disappears as the material goes over more and more to 1,2-polymerized dienes. However, for chemical ruggedness, unsaturation cannot be tolerated. Another course must be chosen. As pointed out in the paper presented by Simha and Schell during the symposium, side chains with rotational freedom contribute to the overall degrees of freedom of the molecule. If the side chains are linear and saturated, they must be long enough to offset the restrictive effect of their presence on the main chain. Certainly, the tertiary butyl pendent group from neohexene does not offer much of a contribution to the ability to rotate. It would be ideal to study a whole family of prepolymer structures of the type illustrated in the lower half of Fig. 11. One might expect the optimum structure to be that in which y and z are as large as possible but small enough to avoid crystalline tendencies.

UNION CARBIDE PREPOLYMER DEVELOPMENT–MICROSTRUCTURE

The Union Carbide investigators developed another approach that will permit investigation, to a limited extent, of the question of improving viscosity and low-temperature properties by means of longer pendent side chains. Preliminary experiments gave promising results [14]. It was previously pointed out that Potts and Ashcraft believed that olefins capable of hydrogen transfer could not be tolerated in this synthesis. However, while trying propylene recently in place of neohexene, these scientists discovered that functionality did not suffer as much as expected. Functionalities of approximately 1.5 in first experiments were encouraging. It is expected that higher pressures will favor chain propagation over hydrogen transfer, and better functionality will be obtained. As a last resort, some type of fractionation may be adopted to improve the functionality of the final product. Preliminary experiments with neohexene copolymers indicate that this may be possible.

The expected improvements in T_g and viscosity are evident in Figs. 12 and 13 [14]. In Fig. 12, the two curves are from neohexene copolymer data. The dashed curve is lower because hydrogen bonding has been

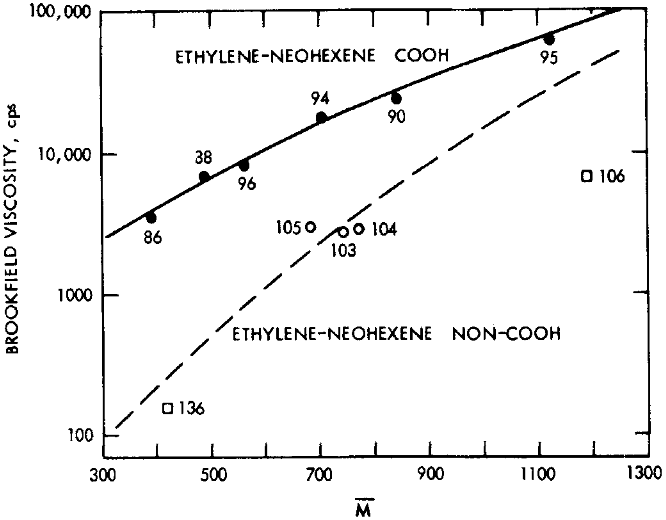

Fig. 12. Viscosity as a function of microstructure (Union Carbide data).

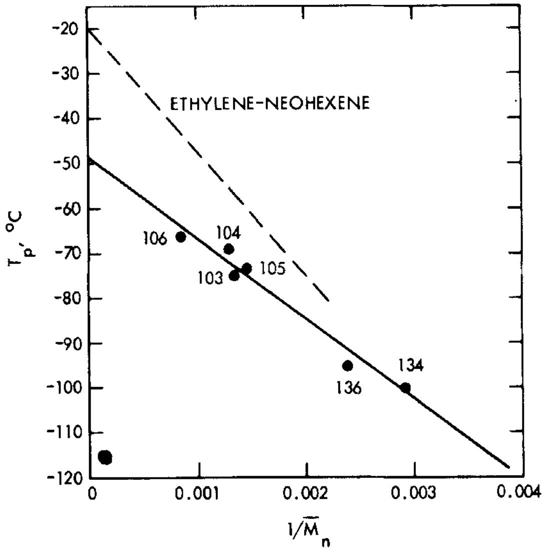

Fig. 13. Low-temperature properties as a function of microstructure (Union Carbide data).

eliminated. Points labeled 103, 104, and 105 are propylene counterparts of the upper curve. The squares (106 and 136), also for propylene copolymers, relate to the lower curve. In general, it can be said that viscosity is lowered by an order of magnitude at the same M_n by substituting propylene for neohexene.

Table 4. Saturated Binder Propellant–Mechanical Properties

Binder propellant	Tensile strength, lb/in.^{2}	% Elongation
Carboxyl-imine	80	75
	140	50
Urethane	140	90
	170	70

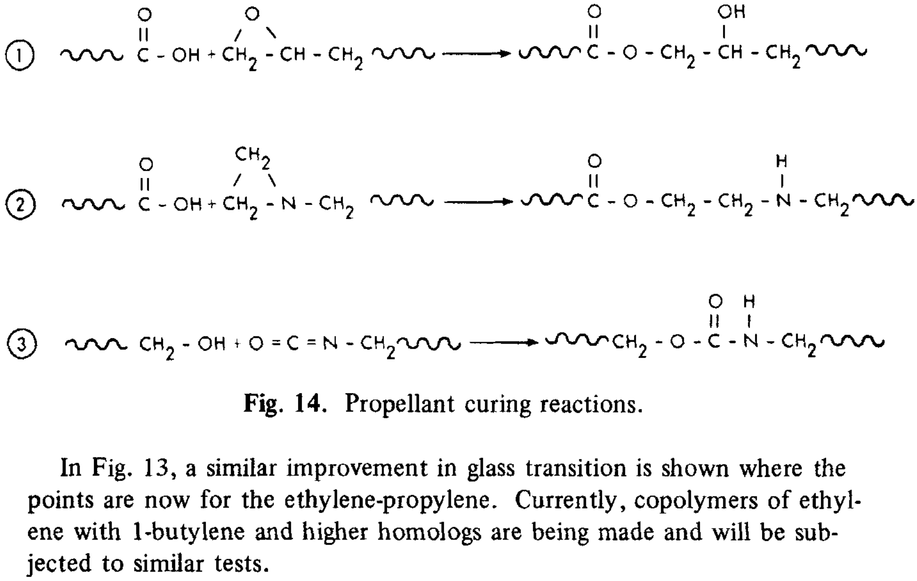

Fig. 14. Propellant curing reactions.

In Fig. 13, a similar improvement in glass transition is shown where the points are now for the ethylene-propylene. Currently, copolymers of ethylene with 1-butylene and higher homologs are being made and will be subjected to similar tests.

CURING SATURATED BINDERS

Figure 14 illustrates the three reactions most widely used today for curing propellants, the formation of ester linkages by the reaction of carboxyls with either epoxides or aziridines (or both), and the formation of urethanes from the reaction of isocyanates with alcohols. Each of these reactions has been used to cure tons of propellant. They are enormously practical, but have their drawbacks. Until something better comes along, these reactions will be applicable to the curing of saturated binders because both carboxyl and hydroxyl functionalities have been achieved in most of the new syntheses and appear to be achievable with the others.

In recent years, urethane cures seemed to be discarded and replaced by the use of carboxyl cures. However, these cures are now regaining some of their popularity. At present, urethanes have two advantages over carboxyls. First, they stand up better under sterilization heating. Second, as presented in Table 4, better mechanical properties are obtained with the urethanes. These data are not representative of propellants in use; however, the higher combination of tensile strength and elongation is typical in equivalent systems. This difference is attributed to side reactions. Both systems suffer from side reactions. However, the type and degree characteristic of epoxides and imines lead to less desirable network structures. Some effort is going on currently to find better curing systems and also to study network relationships.

CONCLUSION

The need for improved solid-propellant binders has stimulated efforts to develop saturated aliphatic castable elastomers. At present, there are indications that new binders beneficial to solid-propellant technology will result from these researches. Saturated-hydrocarbon binders are being used in developing new propellants, and the benefits expected from these propellants are being demonstrated. There is promise also of eliminating, or at least reducing, the major drawbacks encountered with the new materials so that they may be expected to compete with existing binders for general as well as specific uses.

REFERENCES

[1] M. Summerfield, et al., *Astronautics,* 7, 50 (1962).

[2] H. E. Marsh, Jr., and J. J. Hutchison, Jet Propulsion Laboratory, Pasadena, Calif., *Space Programs Summary 37-48,* Vol. III, pp. 95-99, December 31, 1967.

[3] H. E. Marsh, Jr., and J. J. Hutchison, "Functionality Determination Through Flory Network Theory," paper presented at the 3rd ICRPG/AIAA Solid Propulsion Conf., Atlantic City, N. J., June 4-6, 1968.

[4] C. Robillard, W. L. Dowler, J. I. Shafer, and D. E. Udlock, Jet Propulsion Laboratory, Pasadena, Calif., *Tech. Rept., 32-1187,* October 1, 1967 (confidential).

[5] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Plastics Division, Bound Brook, N. J., *Quart. Rept. 1,* February 15, 1966.

[6] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Plastics Division, Bound Brook, N. J., *Quart. Rept. 2,* May 15, 1966.

[7] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Plastics Division, Bound Brook, N. J., *Quart. Rept. 3,* August 15, 1966.

[8] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Plastics Division, Bound Brook, N. J., *Quart. Rept. 4,* November 15, 1966.

[9] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Plastics Division, Bound Brook, N. J., *Quart. Rept. 5,* February 15, 1967.

[10] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Chemicals and Plastics Division, Bound Brook, N. J., *Quart. Rept. 6,* May 19, 1967.

[11] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, Union Carbide Corp., Chemicals and Plastics Division, Bound Brook, N. J., *Quart. Rept. 7,* August 19, 1967.

[12] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, *Saturated Hydrocarbon Polymeric Binder for Advanced Solid Propellant and Hybrid Solid Grains,* Union Carbide Corp., Chemicals and Plastics Division, Bound Brook, N. J., January 19, 1968.

[13] J. J. Hutchison, H. E. Marsh, Jr., and E. F. Cuddihy, Jet Propulsion Laboratory, Pasadena, Calif., *Space Programs Summary 37-49,* Vol. III, pp. 178-180, February 29, 1968.

[14] A. C. Ashcraft, Jr., J. E. Potts, E. M. Sullivan, and E. M. Wise, *Saturated Hydrocarbon Polymeric Binder for Advanced Solid Propellant and Hybrid Solid Grains,* Union Carbide Corp., Chemicals and Plastics Division, Bound Brook, N. J., April 20, 1968.

Accepted by editor May 27, 1969
Received for publication June 16, 1969

Discussion of Paper by H. E. Marsh, Jr.

Recent Developments in Solid-Propellant Binders

M. A. Smook: What initiation system is being used to obtain high functionality with ethylene-propylene?

R. F. Landel (paper presented by Dr. Landel in the absence of Dr. Marsh): This initiation is still AIBN. However, the functionality is now introduced through the chain-transfer process, not from the initiator. As a matter of fact, the problem with the disproportionation of the AIBN radical is still there and this accounts for some of the low functionality in the materials obtained by this process. Hopefully, the continuous reaction will eliminate that source of monofunctional chains.

J. Linsk: Has COOH functionality been attained which is significantly higher than 1?

R. F. Landel: Yes, in Table 3 you see we have a functionality of roughly 0.85 for carboxyl content and 0.85 for the bromine. The bromine can be quantitatively converted to carboxyl, leading to a final functionality of about 1.7.

D. F. Elrick: What was temperature in Fig. 12 concerning viscosity versus M_n for ethylene-neohexene and ethylene-propylene polymers?

R. F. Landel: No temperature was given but it was room temperature.

A. H. Muenker: The reported functionalities of 1.7-1.8 appear reasonably high. It should be pointed out though, that this functionality level may encompass monofunctional polymer components in the order of 20-30 wt%.

R. F. Landel: Yes, this is true, and the problem of functionality has certainly not been solved in these materials. However, it would appear that it ought to at least approach 2 before one considers that he has a potentially valuable material.

P. Throckmorton: Have you studied or have you considered the possible use of saturated cyclic pendent groupings at the backbone for lowering T_g? For example, to achieve this one might copolymerize vinyl cyclohexane into the ethylene-neohexane COOH prepolymer.

R. F. Landel: We have not considered this particular side group, per se. Before going too far in this direction, we would first examine the problems of viscosity and glass temperature jointly. The reason for this is simply that there are too many possible combinations and permutations of side chains, side chain length, and side chain spacing to begin to make a reasonable attack on the question without some prior guidance. Even in a factorial experiment, the number of possible experiments is far too large. The effects of a side chain on T_g and viscosity are related but not identical problems; for example, in comparing the saturated and unsaturated Telagen materials, which differ in viscosity at room temperature by about a factor of 7, one can account for a factor of about 2 simply by the difference in T_g. The remainder is associated with the change in the friction factor. Since these can be studied independently and have somewhat independent effects, we would first propose to examine choice of a side group and its spacing based upon both of these parameters together.