

ELASTOMERS

Chairman

Mr. J. M. Kelble

Speaker

Mr. R. G. Spain

Mr. W. R. Griffin

Dr. W. E. Gibbs

Panel Member

Mr. R. E. Headrick

ELASTOMERS

Dr. W.E. Gibbs

Mr. W.R. Griffin

Mr. R.G. Spain

Directorate of Materials and Processes, ASD

Introduction

The successes by the United States since our last Materials Symposium in 1958, in designing and launching all sorts of manned and unmanned aerospace vehicles could conceivably lead one to believe that all the Air Force problems associated with elastomeric materials have virtually been solved. Unfortunately, or fortunately since this would mean that most of us here today would be out of a job, as the case may be, the requirements for vastly improved elastomeric and compliant materials are still with us. Indeed, elastomers have been, and are still, one of the most environment sensitive of any of the materials of construction and the requirements and environments wherein elastomers are needed to perform for advanced design flight vehicles have become even more stringent. The temperature and pressure range has been even further expanded, the list of fuels, oxidizers, and fluids needing resistant elastomeric seals and sealants is even greater and more awesome, and last but not the least, the research for elastomers resistant to the radiation spectrum has become no less intense.

Appraising elastomer research efforts for the past ten years we could effectively divide the decade into two equal periods. Progress during the period from 1951 - 1956 was most notable and we saw the maximum operating temperature limit for organic elastomeric polymers raised from 250°F to 600°F. Accompanying the significant improvement in thermal stability were vast improvements in chemical resistance and a five to ten fold improvement in resistant to high intensity radiation. Of course, it was recognized even at this time that in so far as temperature stability, 600°F was the ultimate for organic elastomeric polymers. In the ensuing years, 1956 to 1961, no new high polymers have been discovered which have significantly advanced this temperature limitation. All of the meaningful advancements that have been made during the second five year period, in so far as temperatures above 600°F, have been made through the use of design innovations or through the use of unusual resilient composite systems of materials. This does not mean to say that the polymer chemists and rubber industry have been completely stagnant during this time. On the contrary several new hydrocarbon elastomers have reached fruition, including the cis-polyisoprenes, cis-polybutadienes, ethylene-propylene copolymers, and new versions of polyurethanes, silicones, and fluorocarbons, which represent real contributions to the science. Unfortunately, except for a few isolated cases these elastomers do not have sufficient thermal, chemical and radiation stability to fulfill current and future critical Air Force requirements.

As a means of setting the stage for the principal phases of Air Force elastomer research some of the more critical applications and environments in which elastomers will be expected to perform reliably for sustained periods of time are summarized below:

Figure 1. Applications of Elastomers in Aerospace Vehicles

Figure 2. Aerospace Environments

The main part of the program for the Elastomers Panel is divided into three areas portraying a logical, well planned elastomer research program necessary to obtain solutions to the critical problems at hand. The three areas are Synthesis, Characterization, and Engineering.

Synthesis covers the long range program of the Air Force for the preparation of new polymers which may be organic, semi-organic, or inorganic. Primary emphasis will be on polymeric materials which behave in accordance with accepted definitions of elastic behavior.

The second phase, Characterization, is perhaps the least understood and until very recently has received the least attention in research programs for new elastomeric materials. The current approaches used in bridging the gap between the polymer chemist and the elastomer engineer are presented. The steps are outlined whereby the scientist studies the chemical and physical nature of polymers, and transforms them into elastomeric vulcanizates through the use of proper cross-linking agents. The chemical, physical and mechanical properties are investigated in sufficient detail to provide the engineer a feeling for the end use capability. Also, information is fed back at this stage to the synthesis program on any chemical, physical, and mechanical deficiencies in new polymers.

Lastly, Engineering will concentrate on applied research efforts to provide elastomeric materials suitable for fabrication into components as outlined in figure 1 and resistant to the environments detailed in figure 2. One principal difference in this phase is that many of the materials used do not conform to the classical definitions normally assigned to elastomers. Many of the materials would better be described by such words as "resilient," "compliant," "composite systems of materials." In fact, the term "elastomer" as used by the elastomer engineer would better be redefined as any material of construction, organic or inorganic, metallic or nonmetallic, composite or unmodified, used alone or in combination, which is used where an elastomer would normally be used if the environment were favorable.

Synthesis

The synthesis of elastomeric compounds for use in extreme environments has been the subject of considerable Air Force interest over the past several years. The principal problem areas have been (1) thermal stability, (2) solvent resistance, (3) retention of required mechanical properties over wide ranges in temperature, and, (4) radiation resistance, as well as some others.

Certainly significant contributions have been made toward solving these problems. The advent of the fluorocarbon elastomers, for a time, appeared to cope well with the thermal stability requirement. The successive development (figure 3) of the fluoroacrylates 1F4, 2F4, the fluorocondensation polymers, the fluorosilicones, and finally the Viton and Fluorel type fluoroelastomers have pushed the temperature limits increasingly upwards. In a like manner the solvent resistance area was systematically attacked. Elastomers are now available which do a commendable job in contact with conventional jet-engine fuels, hydraulic fluids, and others. Some progress has been made toward the retention of strength at elevated temperature, most notably with the oxide cured acrylate copolymers, as well as resin-cured butyl and ethylene-propylene copolymers. Some progress has also been achieved in the case of elastomers resistant to ionizing radiation, as well as for other lower energy radiation.

However, the progress made thus far has been overshadowed by the increased requirements placed by the design people responsible for tomorrow's weapon and support systems. Whereas a few years ago the maximum temperature limits were 300°F, then 500°F, the thermal limits are now in the over 500°F range and will soon approach 2000°F in some applications. Formerly elastomers were sufficiently resistant to solvents if they showed minimal deterioration in jet fuels and hydraulic fluids. Now the Air Force is concerned with seals for nitrogen tetroxide, and chlorine trifluoride as well as liquid fluorine. Former concern was with elastomers retaining some degree of flexibility and elasticity at -65°F. Now we are entering cryogenic applications for seals and some other application. At the high temperature end, elastomeric compounds are required showing better retention of properties at ever increasing temperatures.

In order to meet these increased requirements, the Polymer Branch and the Elastomers and Coatings Branch of Directorate of Materials and Processes have pursued a program involving both short-range and long-range objectives. The short-range programs will be covered in more detail in the latter portion of this paper.

In the long-range programs, attempts have, and are, being made to study new classes of compounds to gain more knowledge about their properties. In particular, we have devoted some fair degree of effort in systematically studying the formation of polymers from organic, semi-organic, and inorganic compounds. Much of the organic work is devoted to structures which are believed to have a high inherent stability. For example: poly(aromatics), poly(heterocyclics), and polymers with cyclic or ladder type units. These are schematically shown in figure 4. The results of several programs have indicated that the aromatic systems particularly have a high inherent stability. Benzene was found to be stable in the vapor phase to over 1000°F. It is anticipated that other aromatic systems will also retain or improve upon this limit.

The types of polymers of interest to us here differ radically in many cases from the types of structures one commonly thinks of as an elastomer.

One area of work which is familiar to many of you is the polyperfluoroamidine system of figure 5. This system has a relatively good thermal stability, at least when compared with conventional elastomers. Furthermore, it has the unique feature that even after a significant portion of the material has degraded and volatilized the residue is still elastic. The principal disadvantage in the past with this system has been that following the original synthesis, a pyrolysis reaction, the material was highly cross-linked and hence non-processible. An alternate route has been found which again makes the system more attractive. By this method a prepolymer is obtained from a low temperature reaction which may be formed into the desired shapes, then heated at higher temperatures with the loss of ammonia to convert it to the polyperfluoroamidine (figure 6). This polymer apparently retains its enhanced thermal stability, but with the feature that it now approaches a useful material.

During the past year or so a good deal of work has been done on polyaromatic structures. This work was devoted primarily to high temperature fibrous materials, and therefore the polymers are rather rigid structures. Particularly the benzimidazole polymers of figure 7 and others of a similar structure have been found to be quite heat resistant. It is possible that these structures may be modified to yield more compliant materials without too much of a sacrifice in stability. It is also interesting to note that these materials also retain a fair degree of original mechanical properties at high temperatures.

The results of other long-range programs have been disappointing with regard to elastomers. In the semi-organic and inorganic areas very little promise has been found. The materials that have been synthesized are of rather low molecular weight, but it is rather unlikely that significant elastic properties will be realized even when higher molecular weights are obtained.

It has formerly been the general feeling that a gain in high temperature properties should not be accompanied by a significant sacrifice in properties at room temperature. In other words, we have looked at stretching out the plateau of rubber-like elasticity over wider temperature ranges rather than shifting this rubber-like region to higher and higher temperatures with about the same breadth of the elastic region. Perhaps we will now have to concentrate on materials with higher glass transition and crystalline melting temperatures to even approach the required higher performance temperatures.

In addition to the work on synthesis briefly outlined above, some effort has also been initiated on the mechanical properties of representative classes of elastomers to obtain more information about the requirements for retention of strength at higher temperatures, as well as more detailed information on a better explanation of the parameters operating at normal temperatures. Although this work is quite long range it is expected to yield very important information for the future design of compliant materials.

It is the opinion of many concerned with research for new elastomeric compounds, that the design of new elastomers is considerably more difficult than many other forms of polymers such as structural plastics, coatings, even fibrous materials. This is due to the particular combination of properties that elastomers must possess in order to function. In some applications polymers function very well by doing little more than occupying space. Also, they may be filled with types of highly reinforcing materials. These reinforcing materials may actually contribute the necessary strength properties for the application. In elastomers, however, this is not true. The elastomeric compound must show a balanced combination of resilience, modulus, ultimate tensile and elongation coupled with fluid or solvent resistance, generally over a wide temperature range. It is true that for some applications an elastomer need only possess a minimum in perhaps one or two of these properties, but then the other properties must be at a maximum and be retained for considerable times.

As can be seen, the program is not very extensive at this time, particularly regarding synthesis effort. The reason for this is the lack of good ideas for potentially useful systems. Marginal increase in thermal stability coupled perhaps with more significant gains in properties, may be found with better compounding technology for the present day fluoroelastomers. But larger gains in stability and serviceability will come only from new elastomer systems. For the long range programs minor modifications to fluoroelastomers are not of interest. New polymer structures or synthetic approaches to potentially useful polymer structures, which can offer something in stability beyond the fluoroelastomers are of prime consideration.

Characterization

The word elastomer, for purposes of this phase, refers to a compounded vulcanized elastomeric polymer. By this definition the elastomeric polymer or simply polymer is the basic raw material, which is modified or transformed into an elastomer by the addition of vulcanizing agents, reinforcing fillers, and stabilizers, usually followed by the application of heat and pressure to mold a specific shape.

Contrails

You will notice from the discussion of the previous phase, that we are rapidly pushing beyond the thermal and chemical stability limits of conventional polymeric structures. Improved polymers will have different and perhaps very unusual structures, but all will most likely have one feature in common. These materials will be very expensive in terms of money and research time. The price for initial samples of these materials is enough to make one almost forget the need for improved elastomers. Excluding the cost of research to the preparation stage, several thousand dollars per pound is not uncommon. The monomers must often be synthesized by new and unrefined procedures and contribute heavily to this high cost. You can appreciate that new polymers are prepared in small quantities, usually about ten to fifteen grams.

This quantity is sufficient for the initial measurements made by the polymer chemist. However, the situation often arises in which the polymer is worthy of further evaluation as a compounded vulcanized material. The preparation of a vulcanizate and its characterization are usually outside of the polymer chemist's immediate interests and capabilities. On the other hand, few facilities exist where such small quantities of polymer can be compounded, vulcanized into test specimens and used to obtain meaningful data. The obvious economical advantages of working with these initial samples on a micro-compounding scale were recognized by the Air Force and the Elastomers Section has built up a capability in this area. The remainder of this phase will describe the characterization process, the specialized equipment, and problem areas involved.

The purpose of characterization is twofold. First the chemical, physical, and mechanical behavior of possible new elastomer materials must be defined per se and secondly, information and corrective recommendations for deficiencies or undesirable properties must be returned to the synthesis program. This feedback of information is very important. Polymer programs, while directed toward newer and more stable polymeric structures, must also produce useful products. The timely return of information on the deficiencies of a polymer system serve to guide polymer programs so that interesting polymer systems will not be overlooked and effort will not be wasted on those of no promise. The need for improved elastomers, the high cost of research, and the large number of polymer systems demands that characterization be conducted on a micro scale in a thorough fashion.

Elastomeric polymers are rarely used as engineering materials, perhaps because in a strict sense they are liquids. Characterization of an elastomer requires that the thermoplastic polymer be transformed into a vulcanized material. Initial solvent and chemical resistance of vulcanized materials are often indicated by the resistance of the basic polymer, but for the more meaningful data and the host of other properties a vulcanizate is required. The characterization of a new polymer is not always straight forward. Generally, the problems can be grouped into four categories: physical nature of the polymer, reactivity toward cross-linking agents, compatibility with reinforcing fillers, and the need for stabilizers and inhibitors (figure 8).

The first problem area concerns the physical nature of the raw polymer. The most desirable form is a soft thermoplastic gum because conventional equipment and procedures have been established for this form. However, many of the newer elastomers may resemble Teflon at room temperature and possess an elastomeric range above 300° or 400°F. These materials cannot be expected to process on conventional equipment. One approach to this high temperature processing problem involves a high temperature internal mixer with provisions for introducing an inert atmosphere. Figure 9 shows a Brabender Plastograph which can mix at temperatures up to 600°F under an inert gas such as nitrogen. High temperature mixing under inert gases would provide a means of

dispersing fillers and other non-reactive ingredients, but would most likely cause cross-linking agents to react during the mixing procedure. Another approach may be the copulverizing of the hard polymer at cryogenic temperatures with compounding ingredients followed by molding of the resultant powder in compression molds.

Compounding difficulties experienced with new polymers are typified by the perfluoroamidine elastomers. At present, these exist as solid prepolymers. When heated, the solid becomes a liquid of low viscosity, evolves ammonia, and becomes a cross-linked elastomer. One approach is to stop the condensation reaction at a viscous processible gum stage where other compounding ingredients can be dispersed into the polymer in a conventional manner.

Many of these features could be termed deficiencies in the polymer system and a recommendation returned to the polymer chemist for a more conventional physical nature of the polymer. However, poor processing features may be characteristic of the new polymer systems. If of sufficient interest new handling techniques for these materials must be developed.

The second problem is vulcanization of the new polymers. A thorough knowledge of the chemical nature is required before a successful system of cross-linking can be devised. Very often the heat and chemical resistant polymers are also resistant to the chemical action of vulcanization. High energy radiation is often used as a research tool to obtain a vulcanizate without resorting to an exotic chemical system.

Characterization studies are often halted for lack of a good vulcanization system. A good example is the promising elastomeric polymer shown in figure 10. The completely fluorinated copolymer of ethylene and propylene is so chemically resistant that chemical cross-linking systems are not known. Often times this deficiency is relayed back to the polymer chemist and a more reactive monomer is substituted. For example a very similar polymer is shown in figure 11. The tetrafluoroethylene is here replaced with vinylidene fluoride and vulcanization with a diamine and metal oxide system is very rapid. A thought comes to mind - why not place only enough vinylidene fluoride in the polymer for cross-linking and retain the completely fluorinated system with its chemical and heat stability? Unfortunately, the amount of vinylidene fluoride must be in excess of that required for a cross-linked network, otherwise the complete network cannot be formed.

A novel approach to vulcanization is possible with the perfluoroamidine elastomer system. As shown in figure 12, the prepolymer contains amine and imine structures which upon heating to 500-600°F liberate ammonia and condense to a stable triazine structure. If polymerization conditions could be sufficiently controlled so that a polymer with terminal condensable structures could be formed, then the system would cross-link without the addition of an excess of cross-linking sites. This approach would also eliminate the possibility of lowering the heat and chemical resistance of an elastomer by incorporating a less stable cross-linking agent in the network.

The third difficulty, that of a reinforcing filler for new polymers is at present an unsolved one. Carbon black in its many forms leaves much to be desired - especially for the fluorinated polymer systems. Silica fillers were found useful in silicone elastomers but have deficiencies when used with the newer materials. New approaches are needed in this area to obtain optimum mechanical properties with these newer polymers.

The last area involves stabilizers and inhibitors for high temperature elastomers. Naturally, the attempt is to prepare polymers which do not require stabilizers or inhibitors, but to date very few have been made. Polymeric materials are complex and often the idealized structure does not exist. Physical and chemical flaws in the polymer chains are possible weak links. The problem is further complicated with the need for inhibitor action at temperatures which usually degrade even the inhibitor. A study of the inhibiting action of inorganic structures against oxygen may provide leads for these additives. Other inhibitors for chemical attack, catalytic effects, ultraviolet and nuclear radiation, etc., are needed.

In summary, I want to emphasize the importance of timely characterization of new polymer materials. The new polymers, tailor made for the extreme environments encountered in Air Force systems, may be unconventional materials and most likely will require new processing techniques, unheard of vulcanization systems, new reinforcing fillers specially suited to specific polymer systems, and inhibitors capable of 600-1000°F operation. I hope this brief discussion will give an appreciation of the magnitude of the research problems involved in the characterization of new elastomeric polymers.

Engineering

The Elastomers Section of the Directorate of Materials and Processes conducts research for materials which are broader in scope than those described by the term "elastomeric". Many of the materials are better described by such adjectives as compliant, resilient, or flexible. The scope of materials will become evident in the subsequent discussion of this phase.

Certainly one of the major areas of our research concerns materials for use as seals. Current programs are seeking seal materials for anticipated service over a temperature span of about 2500°F and in environments which range from innocuous to that of fluorine gas. The inherent simplicity of elastomeric, or resilient seals is of unquestioned desirability. During initial discussions of sealing problems for systems operating at environmental extremes, these problems are often dismissed with comments such as: "We'll use metal O-rings," "Weld it shut," or "A metal bellows will take up dimensional changes there". Not always, but frequently an opportunity exists to meet the authors of these phrases again at a later date as they inquire of materials suitable for a simple seal, such as an elastomeric O-ring.

In designing elastomeric seals for cryogenic applications, most polymer people are aware as soon as an elastomer is below its glass transition temperature, it is not elastomeric and, hence, cannot effect a seal by overcoming dimensional changes of other members. It is fortunate that not all people are aware of this view. In figure 13, the successful design of a cryogenic seal utilizing elastomeric O-rings is illustrated as currently planned for use on the Centaur. It differs from conventional O-ring seal designs in that no groove is present and a much higher compression of the O-ring is employed. Seals based on fluorinated elastomers, Hypalon, neoprene, and natural rubber have been successfully evaluated at temperatures about 300°F below the glass transition range. It should be emphasized that high compression does not produce effective seals with all types of vulcanizates. Current investigations are directed to elucidation of the effects of polymer structure upon performance as cryogenic seals.

Contrails

For very high temperatures, composite seals utilizing a resilient inorganic fiber skeleton filled with a compliant sealing material have exceptional promise. In a crude analogy, a seal for cold water might consist of a resilient pad of steel wool impregnated with grease. Figure 14 illustrates the performance of a seal based on this concept at rather rigorous conditions. No other types of seals investigated approached this level of performance. The last item of data in figure 14, however, indicates a problem area for this type of seal. The very high compressive forces required to effect the seal preclude use of this concept for low pressure sealing, as for cabin pressurization. At low levels of strain, the corresponding levels of stress are tens of thousands of times those required for elastomeric vulcanizates.

Sealants for both unmanned and manned aerospace vehicles cover an extremely broad area. Sealants are an integral part of the engineering projected for large aerospace vehicles to be launched from the earth's surface. Certainly materials resistant to degradation by the combined aerospace environment of vacuum, temperature, and u.v. radiation are required. The assembly of vehicles above the earth's surface will also require sealants, although the problems become much more complicated. Conventional techniques for sealant application such as refrigeration, mixing immediately prior to use, and carefully controlled curing conditions appear impractical, at best. The activation of sealants by depressurization and by shear is currently being investigated. Perhaps one of the most intriguing problems associated with sealants is the design of a system which will remotely seal the punctures of aerospace vehicles. This area of research is made difficult by the nebulous data available on the frequency and magnitude of punctures which are to be expected. Even if precise data of this type were available, it would appear to be of little comfort to the occupant of a punctured vehicle unless he could use the resultant report to plug up the hole and preserve his vehicle's internal environment.

One concept currently being considered to provide this self-sealing capability is shown in figure 15. Inter-layers of a separated polymeric material and a very active cross-linking agent, which are stable when uncombined, are activated by the mixing occurring on puncture. Silicone and polyurethane polymers which will flow on puncture and will gel on contact with catalytic agents are promising. The major problem of this concept, other than the ever present one of high reliability, is associated with the necessity of a low weight penalty. Apparatus simulating the puncture of aerospace vehicles has been designed and utilized for the evaluation of self-sealing concepts and systems. This apparatus is shown in figure 16; it consists essentially of three connected chambers, the first two of which are evacuated. The third chamber is maintained at atmospheric pressure and is sealed from the second evacuated chamber by the test specimen. By closing a solenoid valve after passage of a 22 caliber bullet fired from a rifle in the first chamber into the central evacuated chamber, a comparatively high vacuum can be maintained on the portion of the test specimen simulating the outer portion of the aerospace vehicle after puncture.

The compactness and light weight of expandable structures appear attractive for both manned and unmanned vehicles. The further capability of rigidization after expansion of these structures makes this concept even more attractive. While a variety of systems currently under investigation are designed to attain rigidization after expansion of the structure to the desired shape, many of these systems would result in only a low degree of rigidization. Rigidity of this type is designed to resist the minor forces resulting from light pressure and the pressure of rarefied atmosphere, and is largely tailored to the demands of satellites comprising parts of communications systems. Some Air Force programs have been largely directed toward obtaining rigidity in a truly structural sense. The general principle is illustrated in figure 17. The flexible, and hence expandable, structure consists of three layers. The outer layer is a fabric externally coated with an

elastomeric coating. The middle layer consists of a fiberglass or similar reinforcing fabric impregnated with a viscous prepolymer. The inner layer is a light weight barrier to prevent adhesion during storage with the structure in a compacted state. Expansion is attained by the release of an inflating gas. All or part of the inflating gas may consist of a reactant which converts the liquid prepolymer to a rigid mass which is reinforced by the fibrous material. Typical gaseous reactants are amines and water vapor. Some estimate of the degree of rigidization obtained in the laboratory can be gained from figure 18 which illustrates such a system described before and after rigidization. Improvements in this concept, or new concepts, are required to improve the temperature capability of the system and to minimize the weight penalty incurred. Silicone and other resin systems may be of promise.

Efforts to develop elastomeric vulcanizates for resistance to elevated temperatures fall essentially into two categories which are exclusive of seals and sealants. The first of these categories embraces vulcanizates which must maintain a substantial degree of strength at elevated temperatures. Projected applications for this class of elastomers would include tires and devices for acoustic and vibrational damping. In these areas the problem is further complicated by the necessity of thermally stable bonding of the vulcanizates to fibrous or metallic substrates. In areas requiring elastomers of high resilience, new hydrocarbon elastomers have shown promise. Figure 19 illustrates a comparison of strengths of vulcanizates, including a natural rubber vulcanizate which is typical of the types used in tire fabrication. Again much higher temperature capability is desired.

The second area of high temperature applications of elastomers involves temperatures which increase by an order of magnitude. Temperatures involved range up to 6500°F, and applications include solid propellant rocket insulation, external rocket insulation, and re-entry drag devices. Problems of adhesion are apparent in all these areas. Certainly criteria of capability of various elastomeric systems over this very broad temperature span is required. Inflated drag devices would additionally require a low permeability to the inflating gas and a higher degree of structural integrity at temperature.

Seals for liquid propellant systems remain a critical problem area. Increases in the energy output of propellant systems have invariably been attended by increases in the chemical activity of the fuels and oxidizers toward seal materials. Further complications arise from the shock sensitivity of seals containing absorbed oxidizers. Yet the simplicity and low weight penalty of elastomeric seals is highly desirable. Particularly difficult seal problems are encountered with chlorine trifluoride, fluorine, and nitrogen tetroxide.

In conclusion, the necessity of close liaison between the applied research programs and the fundamental research areas should be re-emphasized. Guidance is often operative in both directions. Finally, the magnitude of the problems in the area of elastomer research dictates the cooperation of Government, industry, and academic personnel in obtaining solutions.

BIBLIOGRAPHY

1. Montermoso, J.C., "Proceedings Sixth Joint Army, Navy, Air Force Conference on Elastomer Research and Development," 18-20 October 1960.
2. Brown, H.C., "Synthesis of Semi-Organic Fluorine Containing Polymers," WADD TR 59-272, Parts I and II, May 1959 and June 1960.
3. Bartholomew, E.R., Eykamp, G.R., and Gibbs, W.E., "High Temperature Elastomeric Compounds and Polymers," Rubber Chem. and Tech., 32, 1587, 1959.
4. Schwarz, E.G., "The Micro Compounding and Evaluation of Rubber-like Polymers," WADC TR 57-247, July 1957.
5. Spain, R.G., et al, "Research and Development on High Temperature Fuel Resistant Rubber Compounds," WADC TR 55-492, Parts III-VI, 1958-1961.
6. Paciorek, K.L., et al, "Mechanism of Cross-Linking in the Vulcanization of New Elastomeric Polymers," WADC TR 59-129, Parts I and II, July 1959 and July 1960.
7. Jackson, W.W., "Vulcanization of Rubber With High Intensity Gamma Radiation," WADC TR 55-57, April 1955.
8. Smith, F.M., "Development of High-Temperature Resistant Rubber Compounds," WADC TR 56-331, December 1956.
9. Hayes, R.A., "Research on High-Temperature Resistant Rubber Compounds," WADC TR 56-331, Parts II, III, and IV, February 1958, April 1959, April 1960.
10. Kitchen, L.J., et al, "High Temperature Resistant Elastomer Compounds," WADC TR 56-331, February 1961.
11. Sabanas, M., "Composite Inorganic Resilient Seal Materials," WADC TR 59-338, Parts I and II, Oct. 1959, and April 1960.
12. Weitzel, D.H., Robbins, R.F., "Elastomeric Seals and Materials at Cryogenic Temperatures," 1st Quarterly Progress Report, Contract AF 33(616)-61-04, March 1961.

TABLE I

Temperature	Wavelength below which 98% of the energy emitted by a blackbody will fall	Relative Energy
500° F	32 μ	1
1000° F	21 μ	~ 5
2000° F	13 μ	~ 43
4000° F	7 μ	~ 470
10000° F	3 μ	~ 14000

APPLICATIONS OF ELASTOMERS IN AEROSPACE VEHICLES

- Shock & Vibration Mounts
- Flexible Connectors
- Erosion Resistant Coatings
- Thermal Installation
- Radiation Shielding
- Adhesives & Tapes
- Solid Propellants
- Fuel Containers
- Cushioning
- Fluid Seals
- Tires
- Reentry Deceleration Devices
- Structure Seals & Sealants
- Rocket Motor Insulation
- Electrical & Electronic
- Meteorite Self Structure
- Expandable Structure

Contrails

Figure 1.

AEROSPACE ENVIRONMENTS

- Pressure, 10^{-11} mm Hg to 10,000 psi.
- Temperature, -400° to 6000° F
- Radiation, Solar, Nuclear, Cosmic
- Shock and Vibration

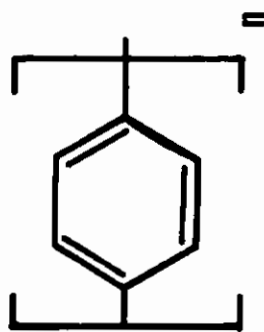
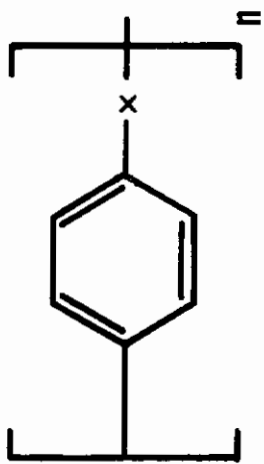
Figure 2.

PREVIOUS WORK

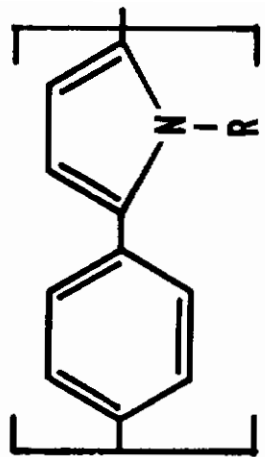
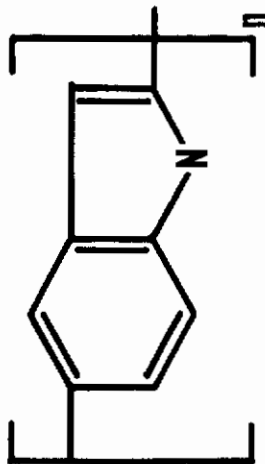
- Fluoroacrylates
- Fluorocondensation Polymers
- Fluorosilicones
- Fluorocarbons

Figure 3.

POLYAROMATICS



POLYHETEROCYCLICS



LADDER POLYMERS

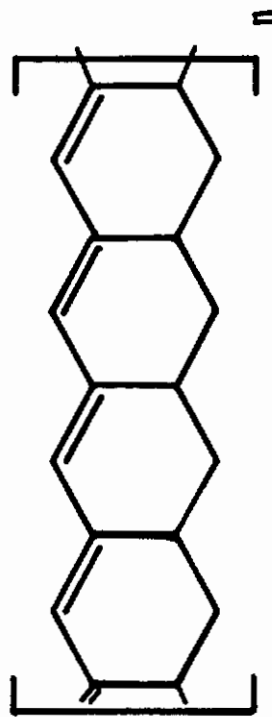


Figure 4.

PERFLUOROAMIDINE POLYMERIZATION

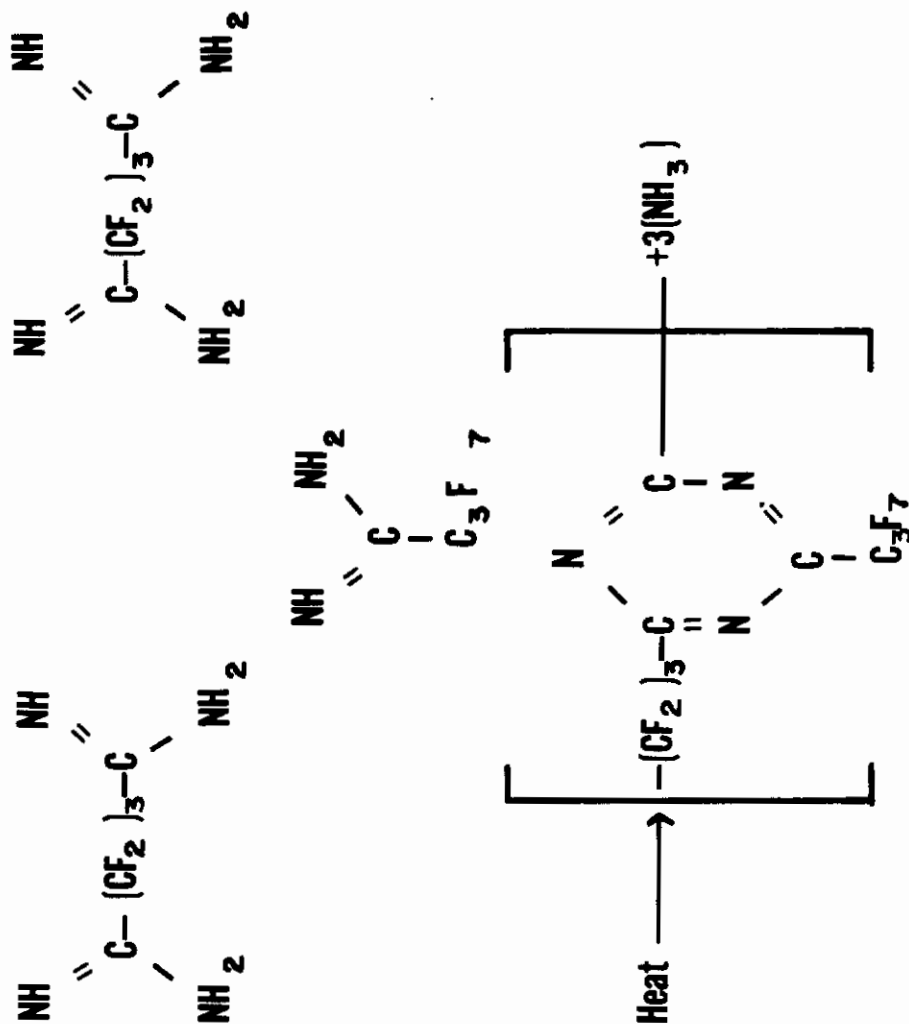


Figure 5.

LOW TEMPERATURE POLYMERIZATION

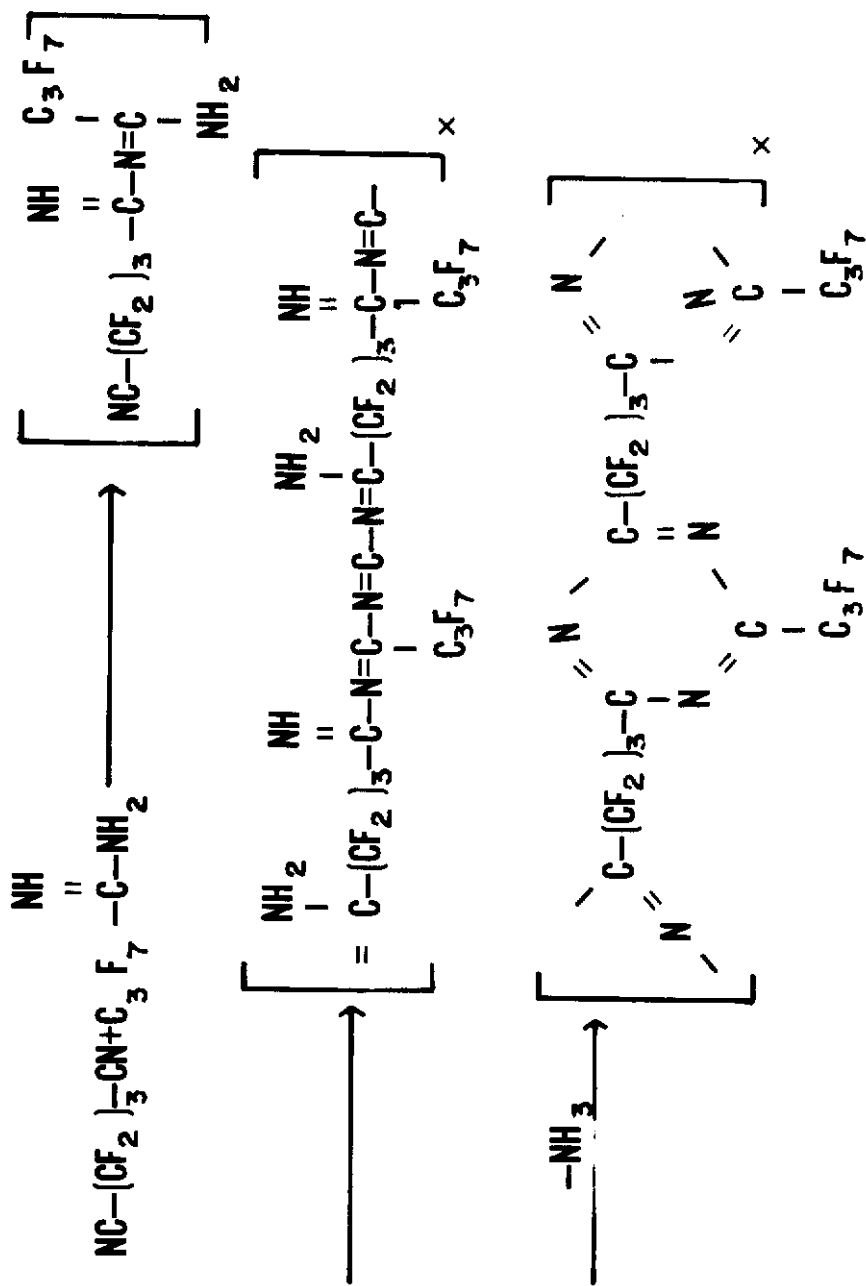


Figure 6.

POLYBENZIMIDAZOLE SYNTHESIS

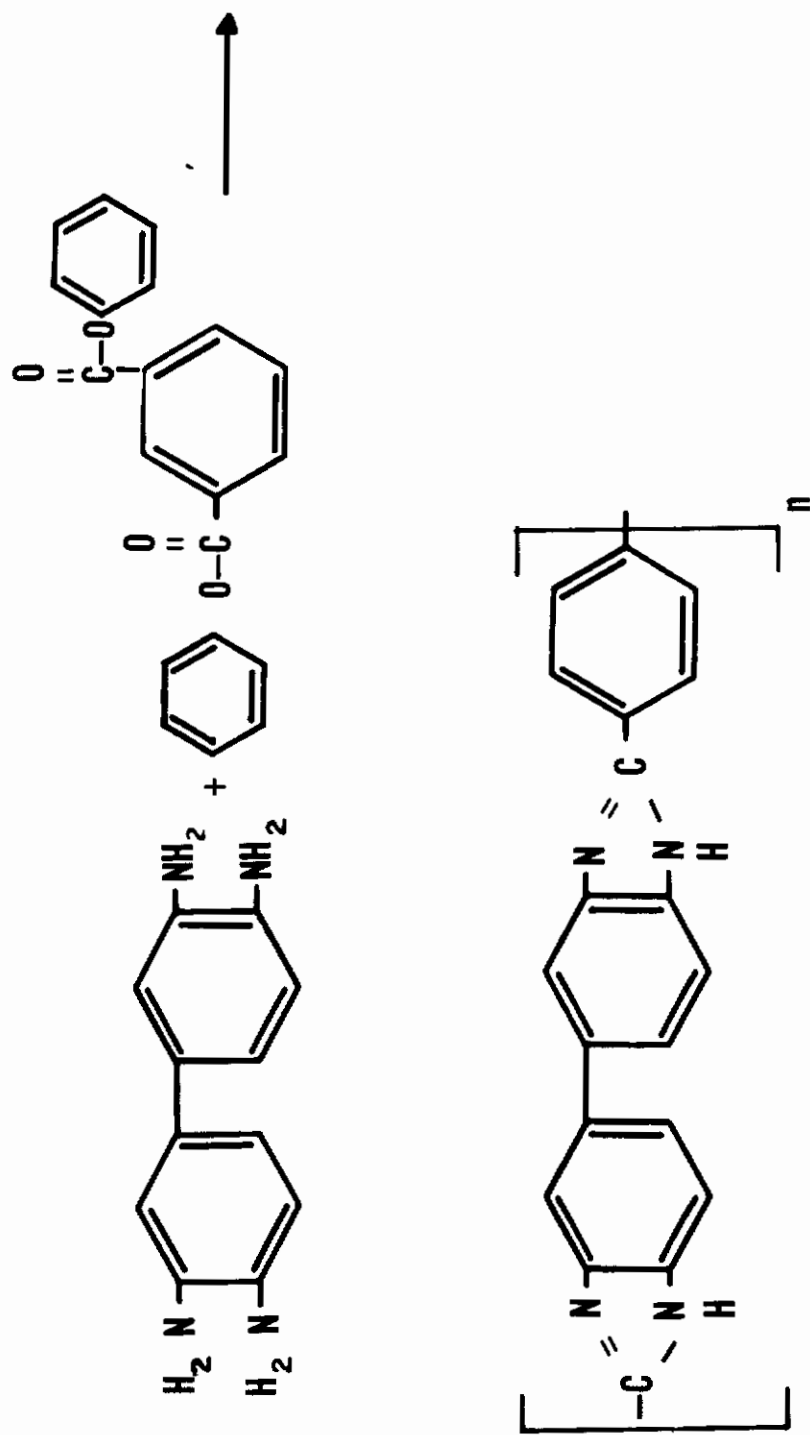


Figure 7.

POLYMER CHARACTERIZATION

- Physical Nature Of The Polymer**
- Reactivity Toward Cross-Linking Agents**
- Compatibility With Reinforcing Fillers**
- Need For Stabilizers And Inhibitors**

Figure 8.

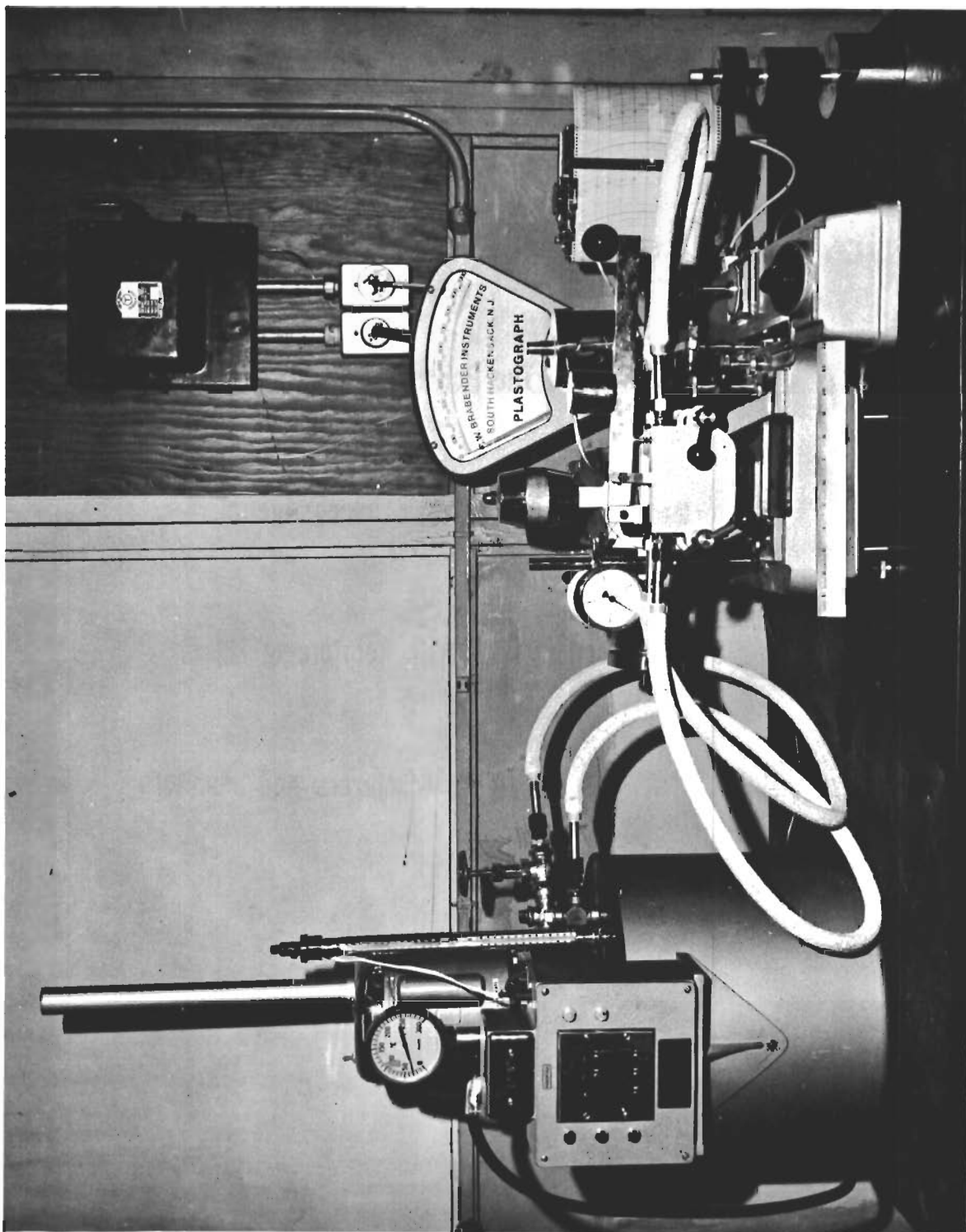


Figure 9.

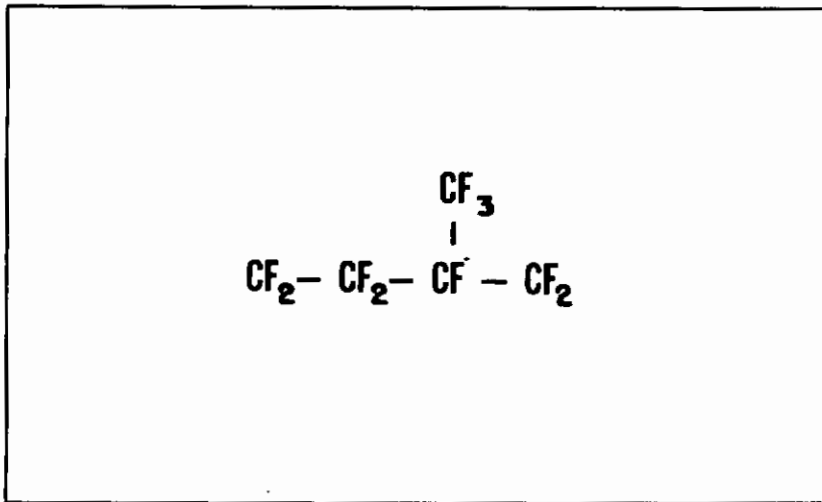


Figure 10.

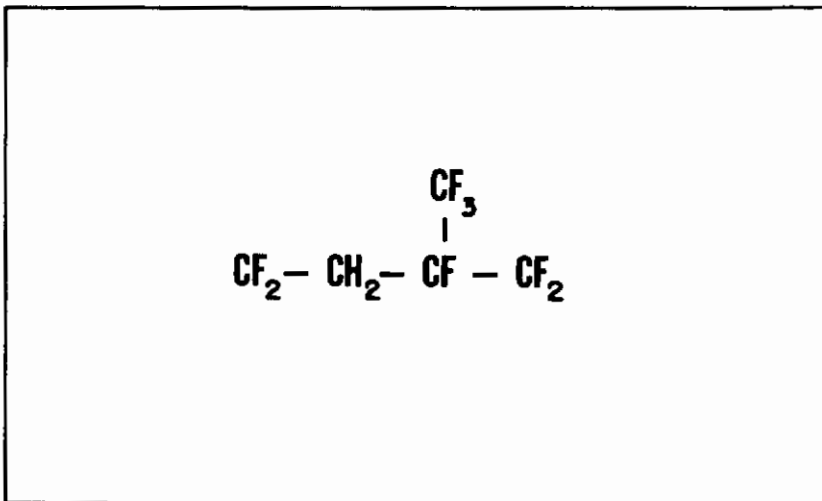


Figure 11.

Contrails

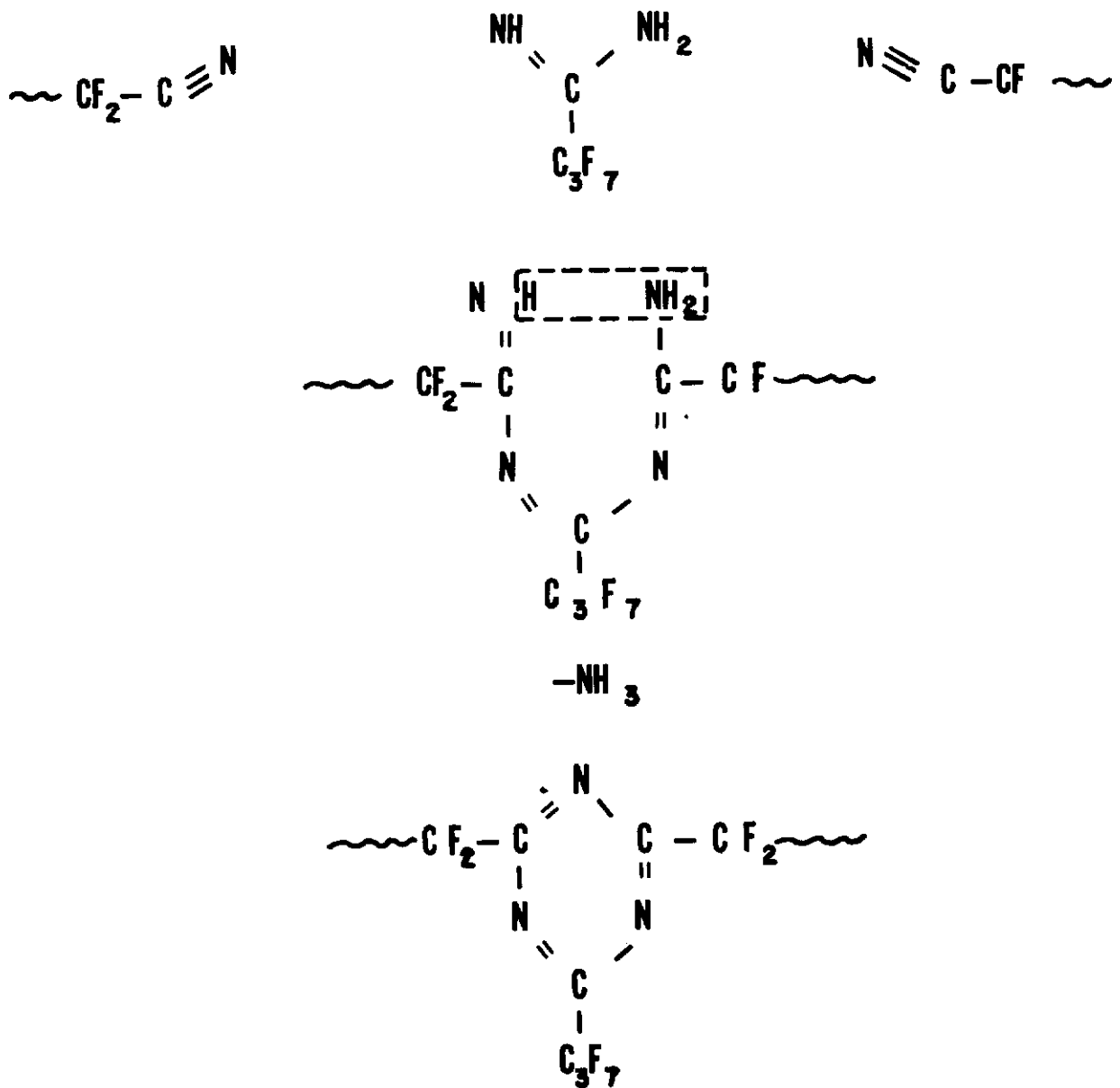


Figure 12.

STATIC O-RING SEALS

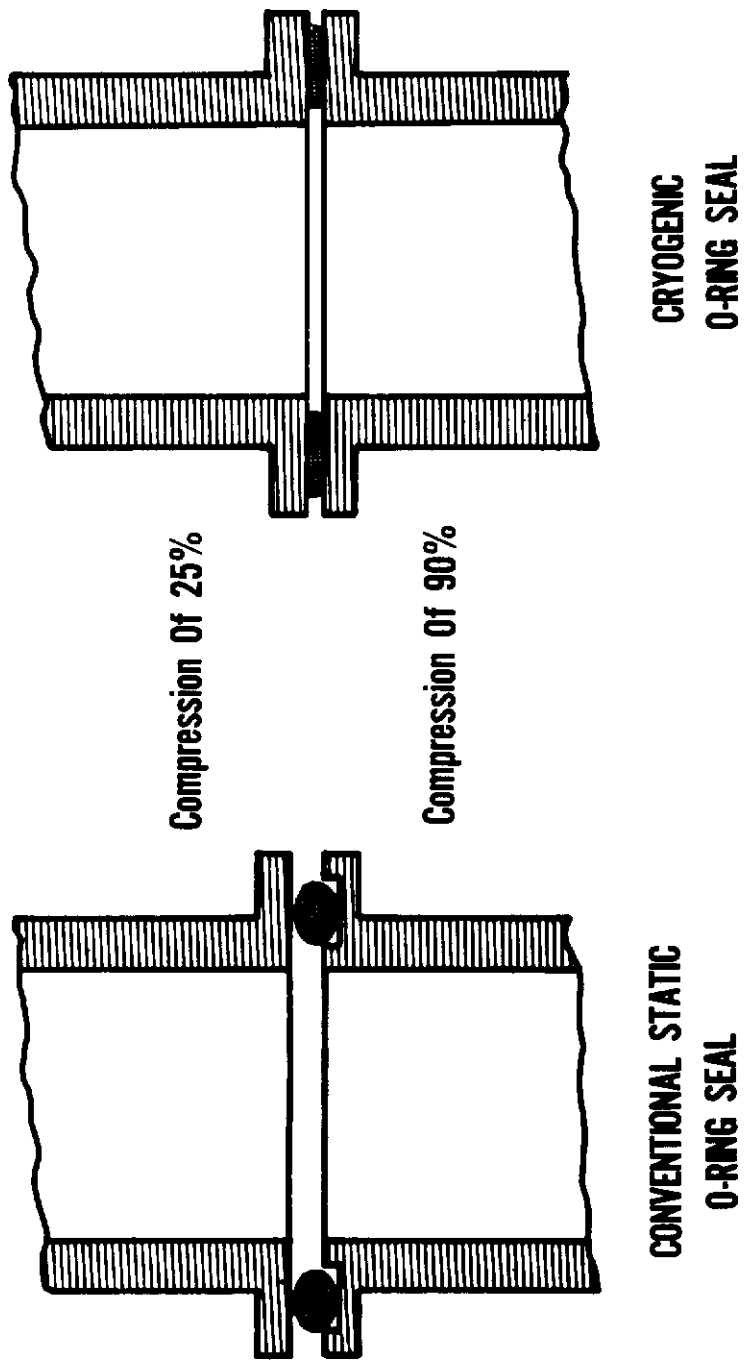


Figure 13.

METALLIC COMPOSITES AS A ROD SEAL

- Type Of Seal Wedge
- Diameter Of Rod 0.5"
- Temperature Cycle . . . 80°F To 1000°F
- Pressure 4000 PSI
- Cycles To Failure 114,000 Dynamic, 6 Thermal
- Force To Effect Initial Seal . . . 350 Lbs.

Figure 14.

SELF SEALANT CONCEPT

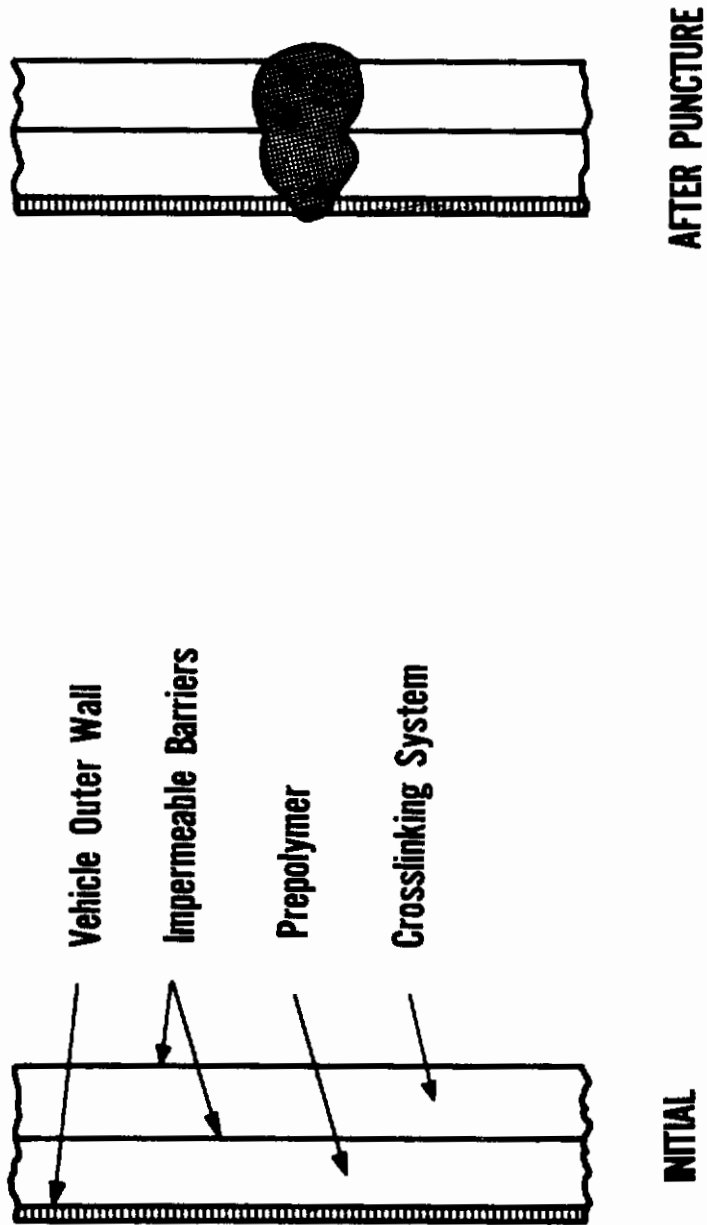


Figure 15.

VEHICLE PUNCTURE SIMULATOR

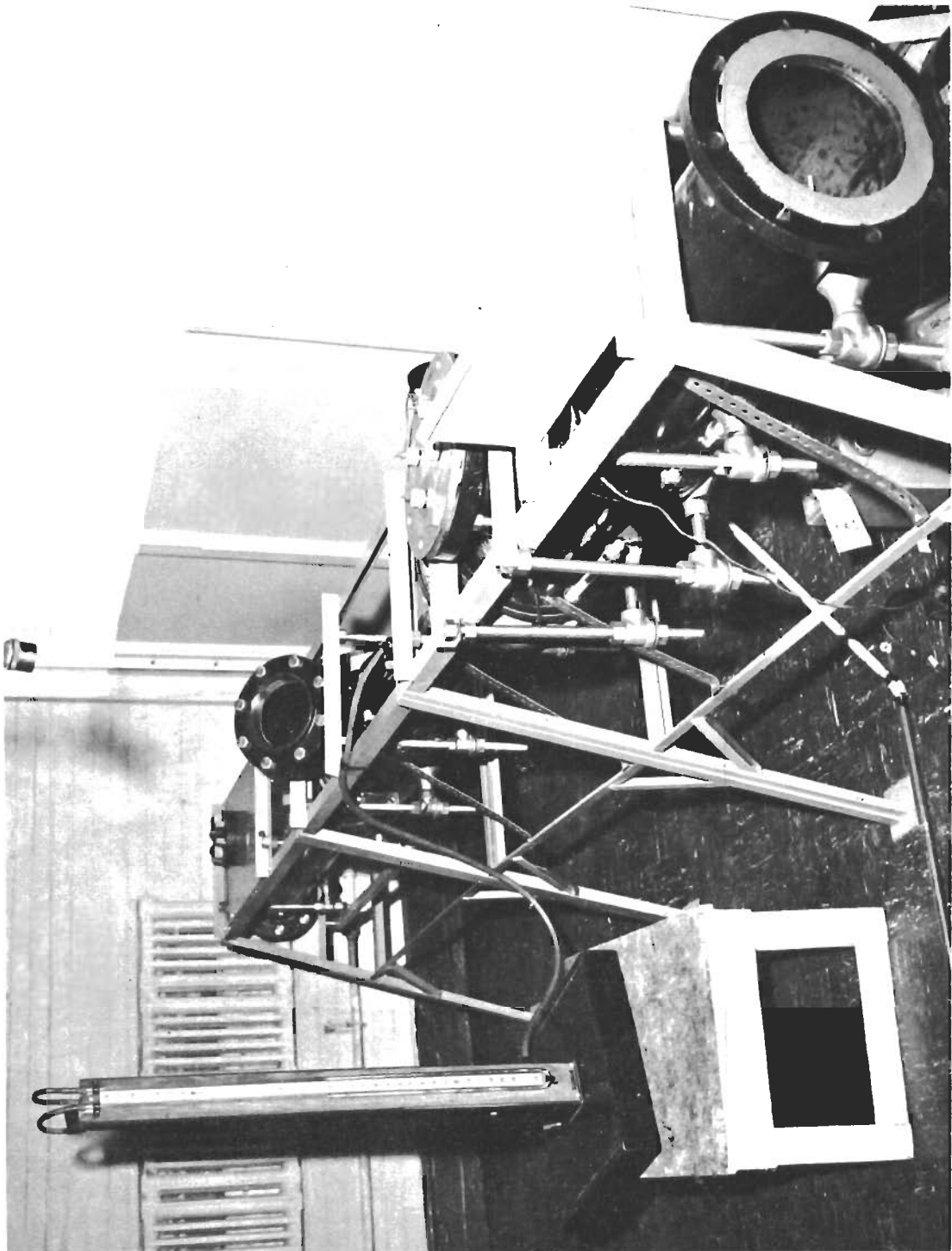


Figure 16.

RIGIDIZATION CONCEPT

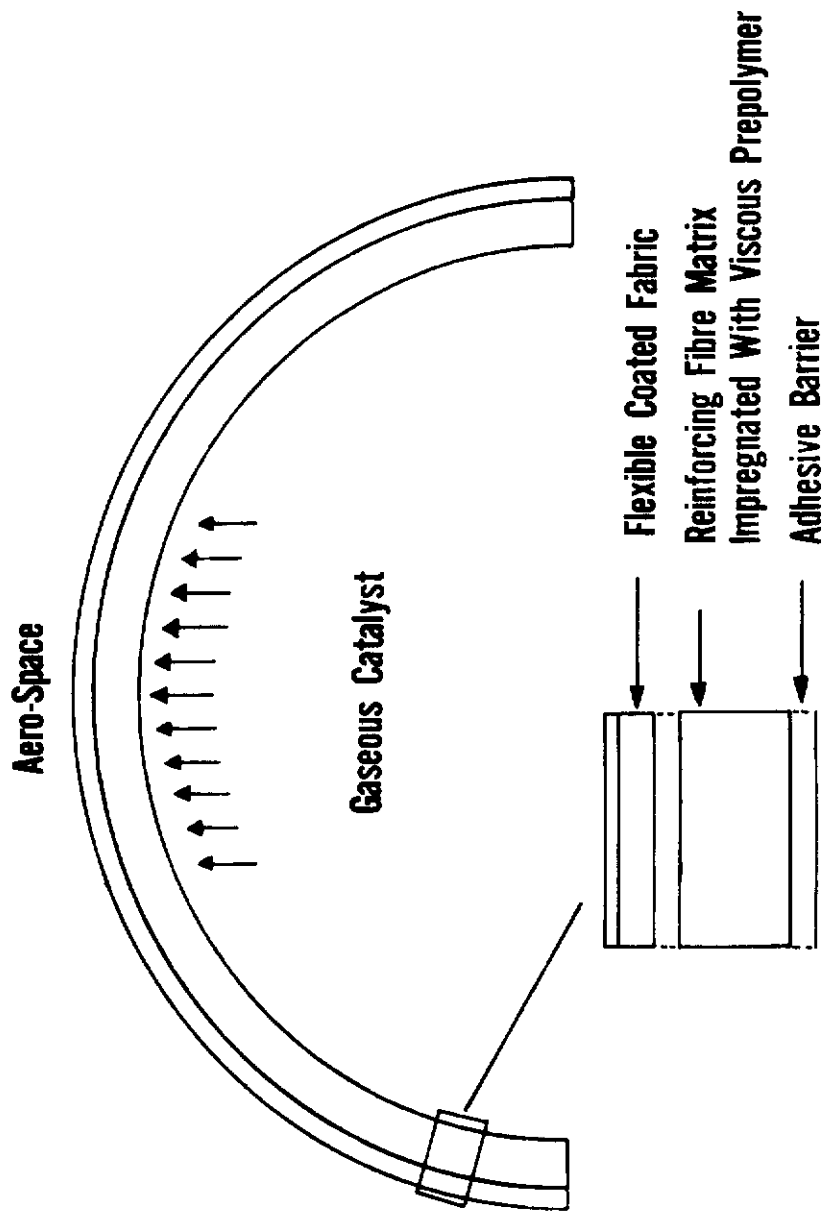


Figure 17.

EXPANDABLE-RIGIDIZABLE STRUCTURE

Span 4.0"
Width 1.0"
Thickness . . . 0.043

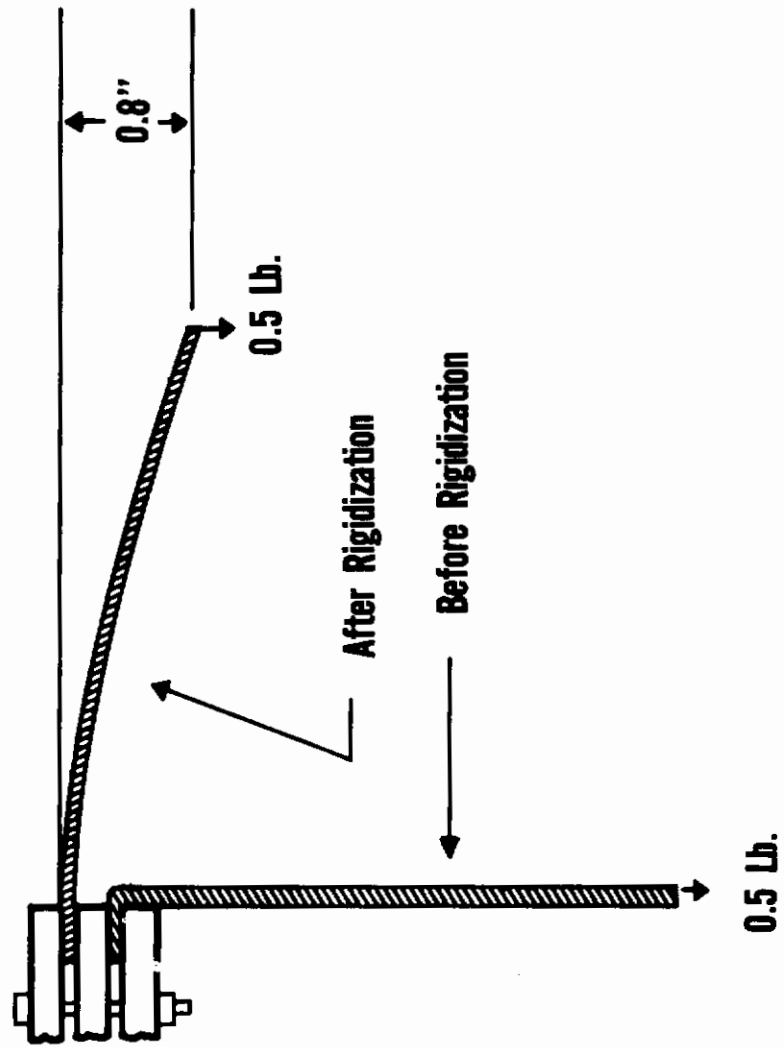


Figure 18.

TENSILE STRENGTHS OF VULCANIZATES

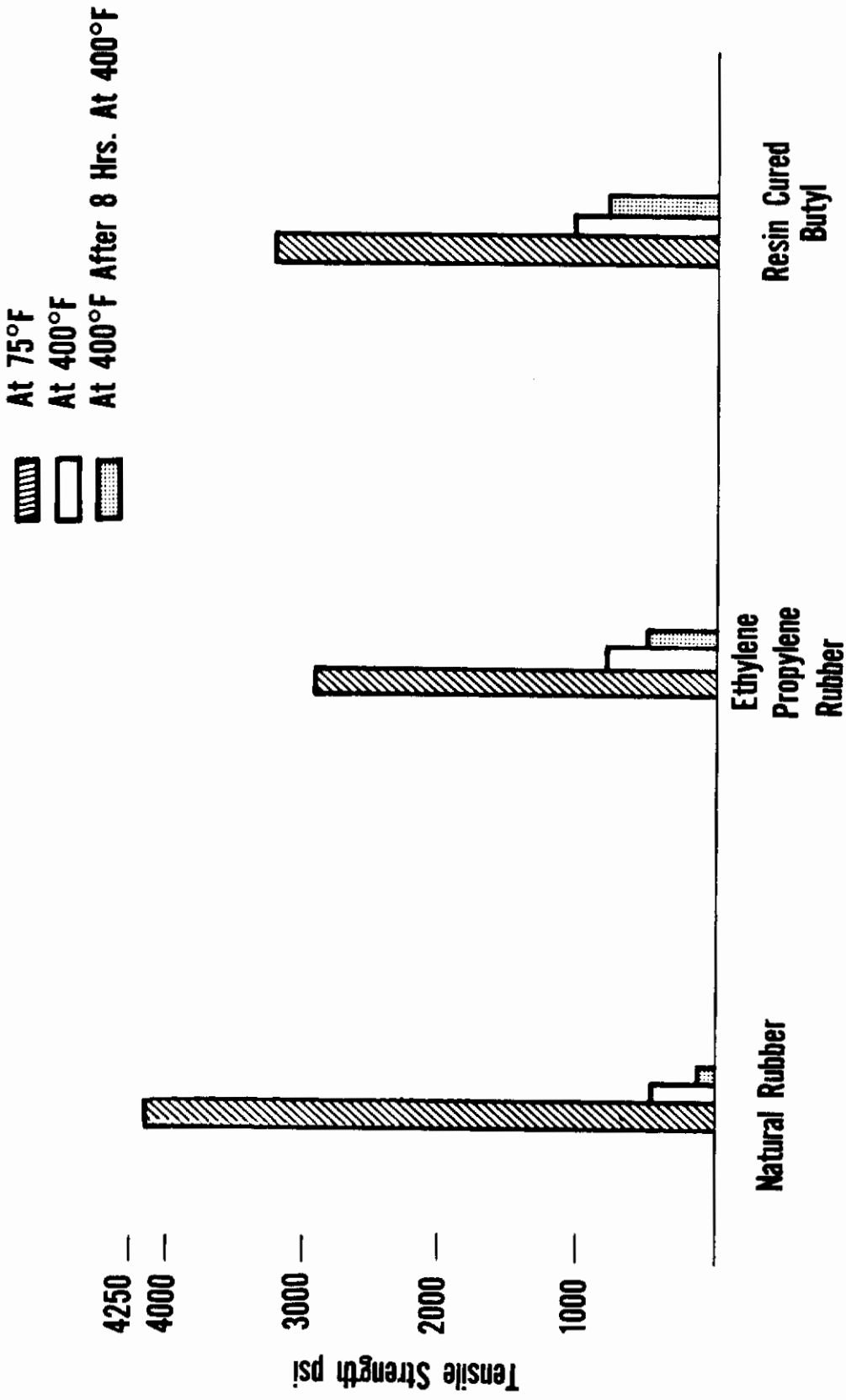


Figure 19.