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Recent Developments in High-Temperature Adhesives

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Introduction

The development of high-speed vehicles after the end of World War II engendered a variety of new problems. Since adhesives have shown their potential in airframe construction, it was realistic to comtemplate their use for the newer aircraft.

As speeds increased, aerodynamic heating became more severe along with the operating temperatures of the propulsion units.

There is a variety of materials that are capable of operating at temperatures in excess of 500°F., but thermal stability alone is only one of many important criteria that must be considered. Limitations such as brittleness, opacity, inelasticity, and high density are commonly found in the heat stable ceramics, glasses, metals, and cermets.

Although the organic polymers could be tailored so as to have toughness, clarity, elasticity, and low density, they were failing to meet the increasing heat stability requirements. Adhesive research began to provide increase thermal resistance but at a severe price in other properties, such as toughness and elasticity. Oxidative degradation was now found to be a factor when high temperature resistance was obtained; thermal softening was found in adhesives that were resistant to oxidation.

The military agencies became cognizant of these problems some years ago and initiated sponsored research to find a solution. Within a span of about five years, it became evident that progress was falling behind design requirements. At this point, concurrent research on semi-inorganic and inorganic polymers got under way. This approach into new areas was justifiable on the basis that the breakthrough potential was good because of the almost nonexistent efforts in this area.

A great deal of progress has been achieved in this research effort, and a solid information foundation is being laid for the ultimate development of the new polymers. Many new problems became evident with semi-inorganic and inorganic polymer synthesis. The most serious ones include: (*1*) the insolubility of the growing polymer chain, which seriously limits molecular weight; (*2*) hydrolytic instability; and (*3*) rapid attack by oxygen.

During this research, the requirements continued to become even more severe and the emphasis was shifted to investigations of ceramic adhesives because of their temperature stability. As a result, research on adhesives useful in the 600–1000°F. range was curtailed. Work in this area vividly demonstrated the thermal and oxidation stability of ceramic adhesives; yet, despite some progress in overcoming brittleness, such adhesives have been entirely too brittle to find wide application.

At the present time it is becoming recognized that research into semi-inorganic adhesive systems on truly unusual organic polymers must be continued even at the risk of the resulting materials failing to function at 2000°F. A good structural adhesive for use at 1000°F. would indeed be a tremendous boon to the advanced design engineers. The research effort and the need for 2000°F. adhesives does not mean that the bonding problems at 600–1000°F. have been solved.

With the coming of supersonic jet transports and space stations, another set of requirements has been born. The expense of building such structures and the long service life envisioned for such items means that there is a need for structural adhesives useful at about 500°F., not for a mere 192 hr., but for a minimum of 30,000 hr. to about five years. Just as missiles introduced the need for very high temperature adhesives for very short exposure times, there will be a need for very long service life at lower temperatures.

Our present knowledge of organic adhesives and our recent findings on semi-inorganic polymers make these areas of research particularly attractive. An increased effort along these lines should start at once. It is doubtful if there are any extensive data on the aging characteristics of adhesives for periods up to five years at temperatures

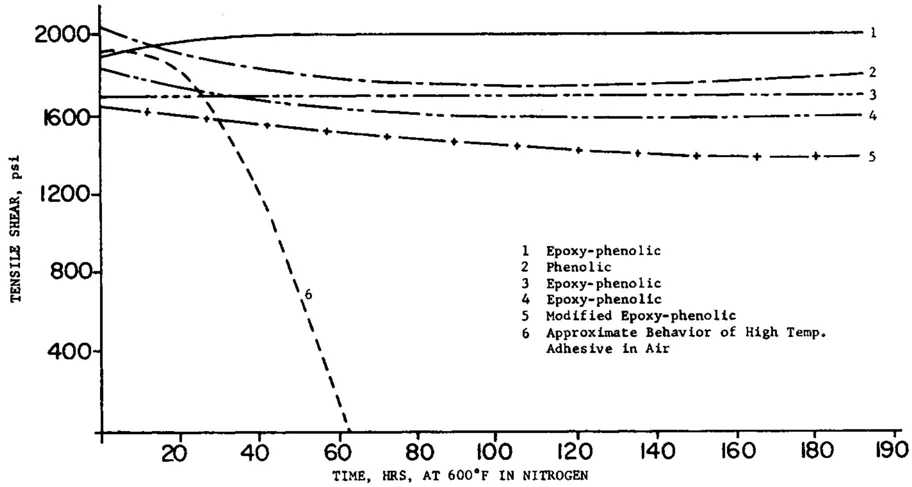

Fig. 1. Commercial adhesives. 600°F. tensile shear vs. 600°F. exposure time. 17–7 PH stainless steel. Phosphate etch.

ranging from 180–500°F. An even more vexing problem is the testing of such adhesives; experience has shown that it is extremely unwise to attempt a prediction of an adhesive's behavior over a long time span, based upon accelerated test data obtained at a higher temperature.

Discussion

Some preliminary remarks are pertinent here. Although Narmco is actively engaged in high-temperature adhesive research, an attempt was made to obtain data from military agencies and manufacturers. This was done because this would present a more complete picture on developments in this area and because it might appear presumptuous to present only Narmco data. Unfortunately, all replies but one were negative. As a result, virtually all of the data presented will be those from our laboratory.

Ceramic adhesives have been excluded from this presentation because the writer has specialized only in organic materials.

The work on high temperature adhesives was arbitrarily divided into four categories based on environmental conditions: (*1*) very short exposures (less than 2 min.) at temperatures over 1000°F.; (*2*) very long exposures (1 yr.) at temperatures below 500°F.; (*3*) long exposures (1000 hr.) at 500°F.; and (*4*) short exposures (1 hr.) at 700–1000°F.

Very Short Exposures at Temperatures over 1000°F.

The use of rockets and missiles, which have short lives and exposures to very high temperatures, necessitated development of adhesives capable of functioning under these new conditions. As a first step in the development of such materials it was necessary to evaluate currently available adhesives.

Testing under these conditions required a means of rapid heating to a controllable temperature. With quartz lamps, temperatures up to 1500°F. could be achieved in 1 min. and held within acceptable limits.[1]

At such high temperatures, a complicating factor was envisioned. Would degradation of the adhesive be due to oxidation only or would purely thermal effects enter into the behavior, or would both effects be found? It has been known for some time that adhesives suffer little loss in strength when exposed to elevated temperatures in an inert atmosphere (see Fig. 1). The broken line indicates a typical curve for such systems in air. There was very little difference in the data under conditions of air and nitrogen.[1] This is interpreted to mean that at temperatures from 1200 to 1500°F. with rapid heat-up, pure thermal energy is sufficient to cause rapid degradation of the polymer system, and that this effect is essentially equivalent to the combined effects of air and heat.

From the work just shown, one phenolic system was selected as having the best properties and research concentrated upon this adhesive. One phase included the evaluation of various fillers. These data are shown in Figure 2. All formulations had essentially the same tensile shear strength at 1500°F. except one, which had 137 phr of strontium carbonate added and bonded to steel that was etched with hydrofluoric-nitric acid. There were two other points of interest in these data. First, it was unusual to note the increase in strength, in most formulations, from 1250 to 1500°F.; this is apparently a genuine phenomenon because it was found repeatedly with various formulations in individual test specimens of a series, and because some of the tests were repeated and the same effect noticed with unusually good test data scatter.

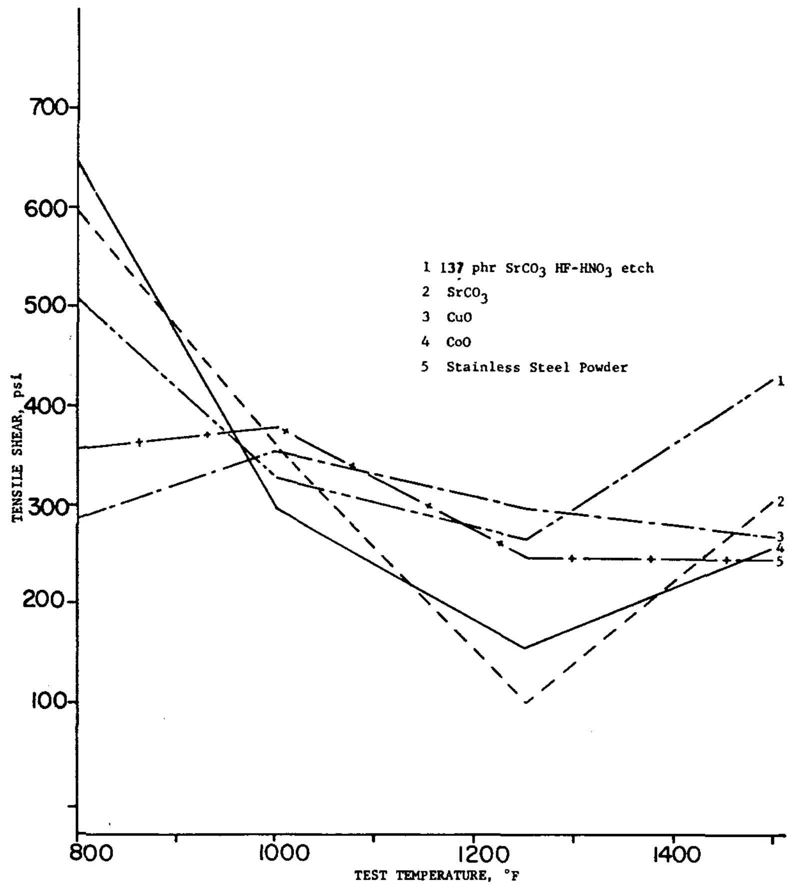

Fig. 2. Phenolic with high values for filler systems.

Second, it was somewhat surprising that copper oxide and stainless steel powder failed to promote more rapid destruction of the adhesive due to their catalytic effect on oxidation.

These data were interesting for another reason because they indicated that a tendency has developed to automatically exclude organic systems when temperatures in excess of 1000°F. were present. It is known that adhesive deterioration is a function of temperature *and* exposure time; this must be considered in all cases because this is due to decomposition kinetics with which we have to live.

Very Long Time Exposure at Low Temperatures

There exists today an active program to design supersonic jet transports and passenger aircraft. These items will be very expensive and must be usable for long periods of time with the reliability found in present aircraft. Obviously, the use of structural adhesives would be most desirable. Unfortunately, there are lacking any data on adhesives concerning such long time exposures at temperatures from 250–500°F. The usual range of exposure time is 192–200 hr. at temperature, and occasionally there are some data up to 1000 hr. For these new aircraft, it is necessary to design for at least a useful life of 30,000 hr., or somewhat over three years of flying time.

It has been found that it is impossible to predict adhesive behavior over a protracted period of time at a given temperature by accelerated tests at

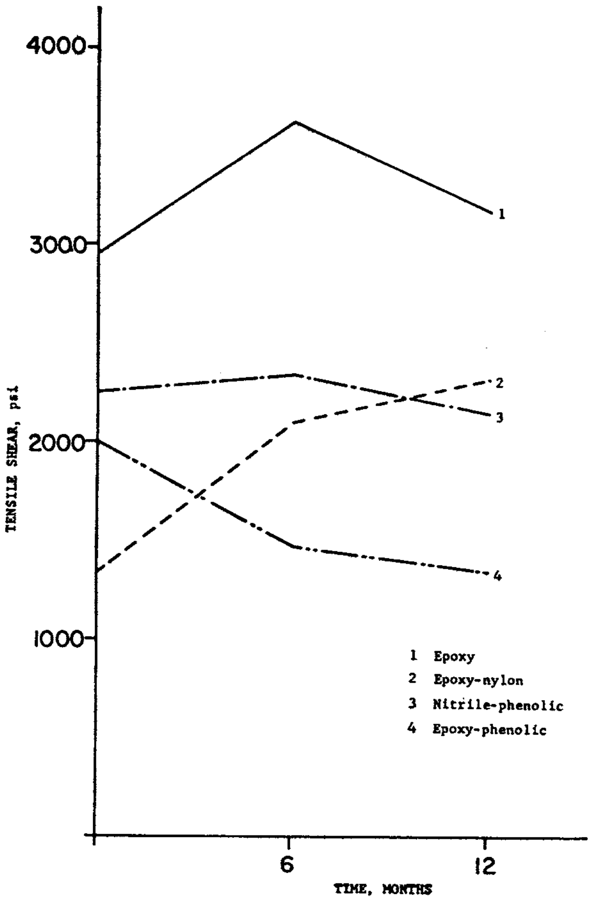

Fig. 3. Tensile shear effect of exposure at 250°F.

some higher temperature. Such a procedure brings into play different kinetics and can result in different decomposition mechanisms.

Last year, a program was started at Narmco to evaluate commercial high temperature adhesives at 250 and 350°F. The length of this test will be five years. This is the only evaluation method available today because there are no accelerated reliable tests available.

This is a deplorable situation because if present adhesives cannot meet the requirements, new materials will have to be developed, but it will take three years to obtain data. A vigorous research program is required for development of reliable accelerated tests for a variety of physical properties such as tensile shear, tensile strength, peel strength, properties on honeycomb construction, and exposure to fluids. Without these tests, the development of a reliable Mach 3 transport can be delayed.

Four types of adhesives were used in this evaluation study. Each was selected as typical of its type. Bonds were prepared on aluminum because of the exposure temperatures. For exposures at 500°F., stainless steel bonds should be used. Figure 3 illustrates the data after one year at 250°F. and, with the exception of the epoxy-phenolic, are performing in a fairly satisfactory manner. However, it was somewhat depressing to find that the epoxy-phenolic, which is a 500°F. adhesive of the 422 type, is showing the poorest performance. Yet, further data must be obtained because it is impossible to predict future behavior. Perhaps one adhesive will improve in tensile shear from now on; extrapolations are impossible with our present knowledge.

The data on the high peel strength epoxy-nylon adhesive were a surprise because of its almost doubling of tensile shear strength. The low initial value is due to the fact that this is an adhesive for use up to 180°F. Just how long this strength can be maintained is unknown.

The test data obtained after one year at 350°F. demonstrated even poorer performance. Once more the 422-type epoxy-phenolic suffered the greatest loss in strength, while the nitrile-phenolic was surprisingly good. These data are illustrated in Figure 4.

Here we can see an area of research which demands a great deal of effort. At present, we are almost completely devoid of knowledge in all aspects of adhesive behavior over very long time spans. While the prognosis is good for achieving adhesives for very short time intervals at very high temperatures, the picture with our present knowledge for a five-year adhesive is indeed a gloomy one. So far we have considered only tensile shear

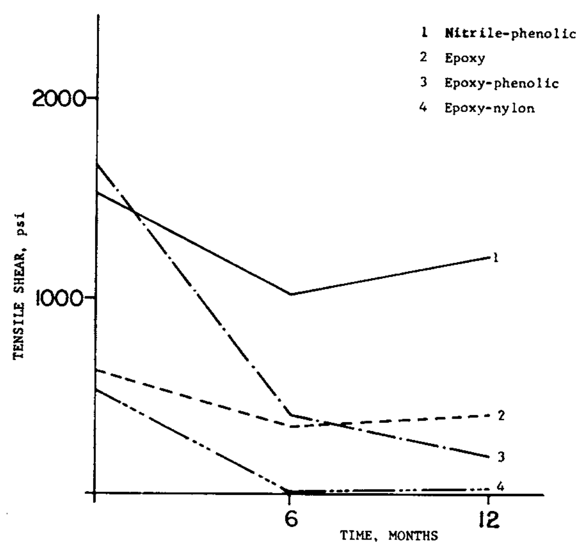

Fig. 4. Tensile shear effect of exposure at 350°F.

at 250 and 350°F., but how about present adhesive behavior at 500°F., behavior under a constant or cyclical load, exposure to water vapor, various fluids, subzero temperatures, and fatigue tests? Will we have to run each test for 30,000 hr. on present materials? Will we have to evaluate each new adhesive for 30,000 hr. also for each of the above tests?

Long Exposures at 500° F.

One of the largest advances in adhesive technology came about with the development of the 422-type 500°F. adhesives useful for 192 hr. at this temperature. However, it was soon found that these data could not be reproduced when tests were made in air and on stainless steel instead of on aluminum.

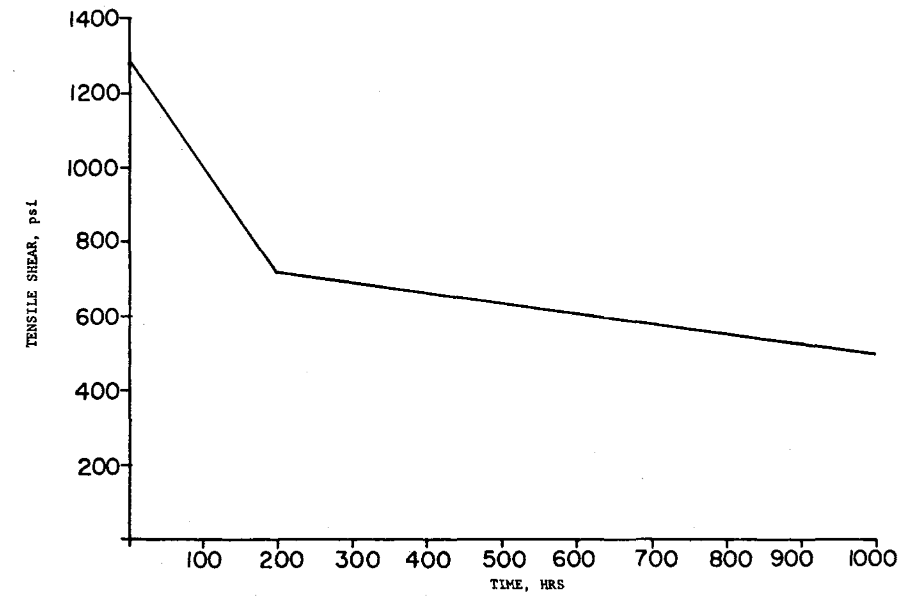

Fig. 5. Tensile shear at 500°F. epoxy-silicone-phenolic adhesive. 17–7 PH stainless steel. Phosphate etch.

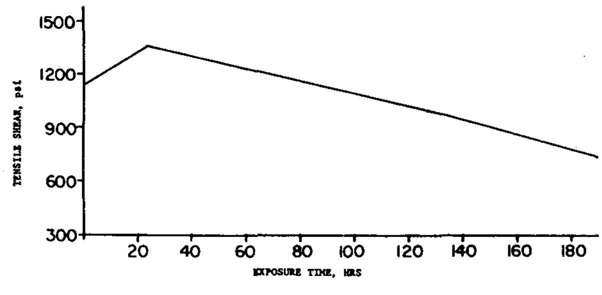

Fig. 6. Tensile shear strength epoxy-silicone-phenolic adhesive aging and testing at 600°F. 17–7 PH stainless steel. Phosphate etch.

About two years ago, Narmco[2] developed an adhesive that successfully adhered stainless steel to itself for 1000 hr. at 500°F. This adhesive gave 720 psi after 192 hr. and 520 psi after 1000 hr. at 500°F., thus showing a remarkably slight slope (see Figs. 5 and 6). In one other respect was this adhesive novel; it contained arsenic pentoxide as a curing agent. Subsequent work at Narmco[3] showed that this adhesive was semi-inorganic in nature and contained the unusual Si-O-As^{+5} linkage; further, the epoxy novolac component was cured to a polyether rather than by the usual polymerization to the less heat stable secondary hydroxyl groups. The development of this semi-inorganic adhesive was also a major accomplishment, which potentially represented the first step toward semi-inorganic adhesives with improved properties resulting either from better thermal stability or improved oxidation resistance.

As a result of this work, a new approach to semi-inorganic polymers was started. Rather than attempting the polymerization of semi-inorganic monomers, the method consisted of the reaction of heat stable organic polymers with inorganic reagents. By this route, the final product would be of high enough molecular weight to be useful and obviate the difficulty of having the growing semi-inorganic polymer precipitate before the proper molecular weight range was obtained.

Continued work at Narmco[3] on semi-inorganic

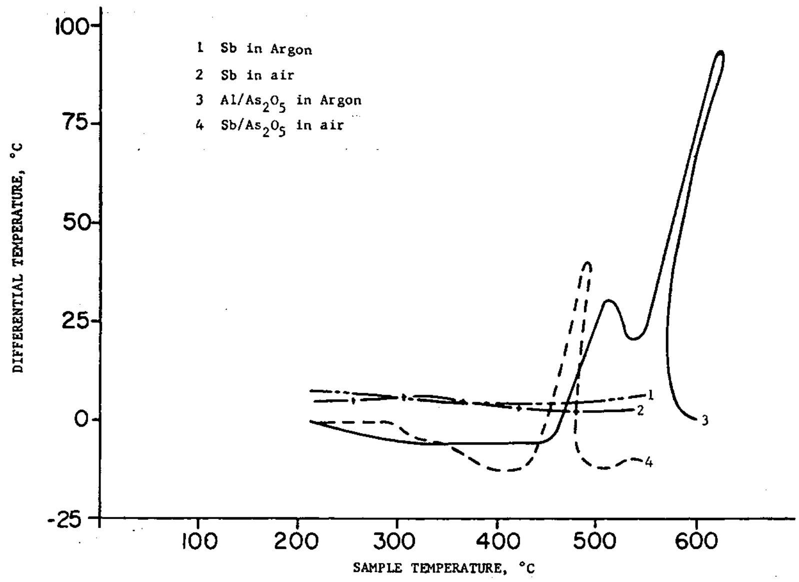

Fig. 7. Differential thermal analysis (performed at NOL laboratories).

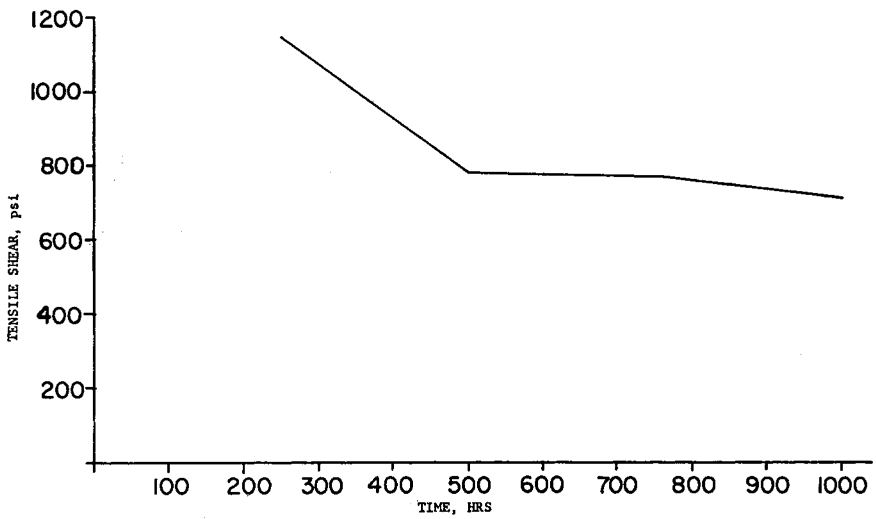

Fig. 8. Newest epoxy-silicone-phenolic tensile shear at 500°F. in air. 17–7 PH stainless steel. Phosphate etch.

polymers and adhesives has demonstrated that this semi-inorganic adhesive fails at 1000°F. apparently because of a thermite reaction between the aluminum filler and the arsenic pentoxide (see Fig. 7). If one wishes to use the arsenic pentoxide, it will be necessary to use some filler other than aluminum for use at 1000°F.

Recently, under a continuation of the same Navy program,[4] a new adhesive was developed which had improved properties at 500°F. The structure of this adhesive is currently under investigation but is proving to be a very complex problem. However, Figure 8 illustrates its properties for up to 1000 hr. at 500°F. This adhesive has a tensile shear strength of 1700 psi at room temperature and exhibits an excellent retention of properties from 500 to 1000 hr. The value of 1150 psi after 250 hr. at 500°F. is high enough to be considered for structural purposes provided other physical values, which have yet to be evaluated, are acceptable. In its present state of development, this adhesive requires a high-temperature cure schedule. The schedule requires 3 hr. at 600°F. with a 24-hr. post-cure at 550°F. Such a cure cycle would seriously damage most organic adhesives. With a 2-hr. cure at 350°F. the adhesive exhibits tensile shear values of only 850 psi after 10 min. up to 5 hr. at 550°F. and then continues to increase to 1300 psi after 50 hr. at this temperature. If data were collected at 500°F. up to 250 hr., the cure in Figure 7 would exhibit a rapid increase in tensile from about 10–24 hr. up to some point short of 250 hr. If the initial low values are acceptable, then a normal cure schedule could be used. This adhesive has been put into the five-year exposure test at 250 and 350°F.

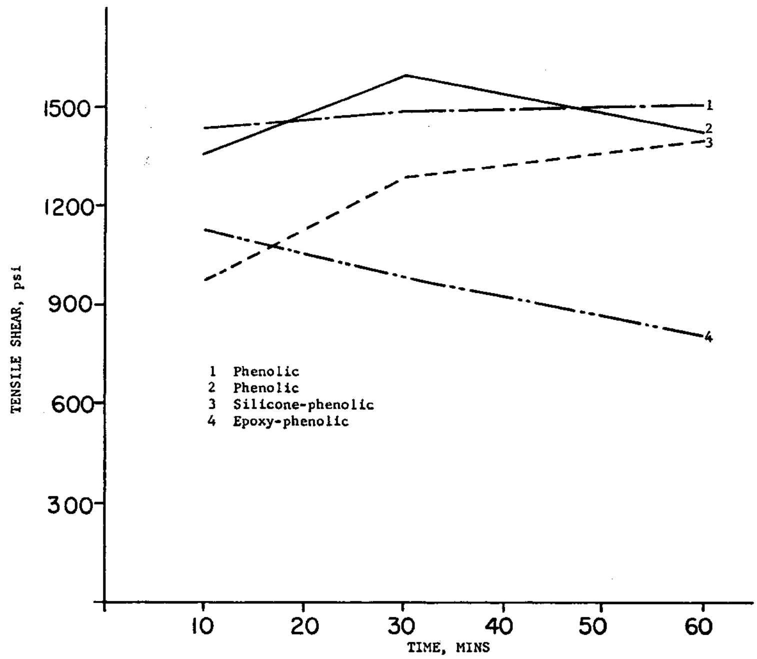

Fig. 9. Tensile shear, 700°F. 17–7 PH stainless steel. Phosphate etch.

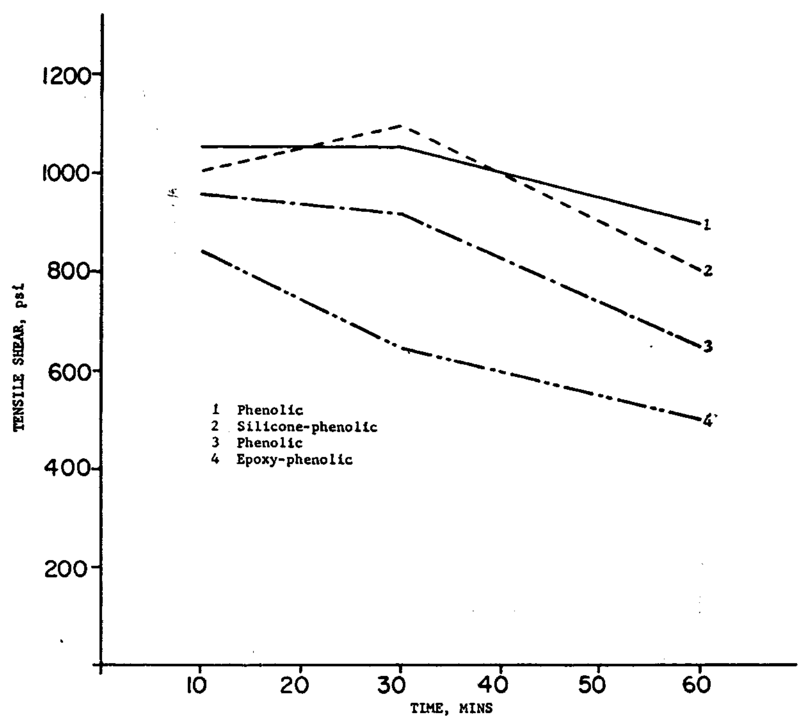

Fig. 10. Tensile shear, 900°F. 17–7 PH stainless steel. Phosphate etch.

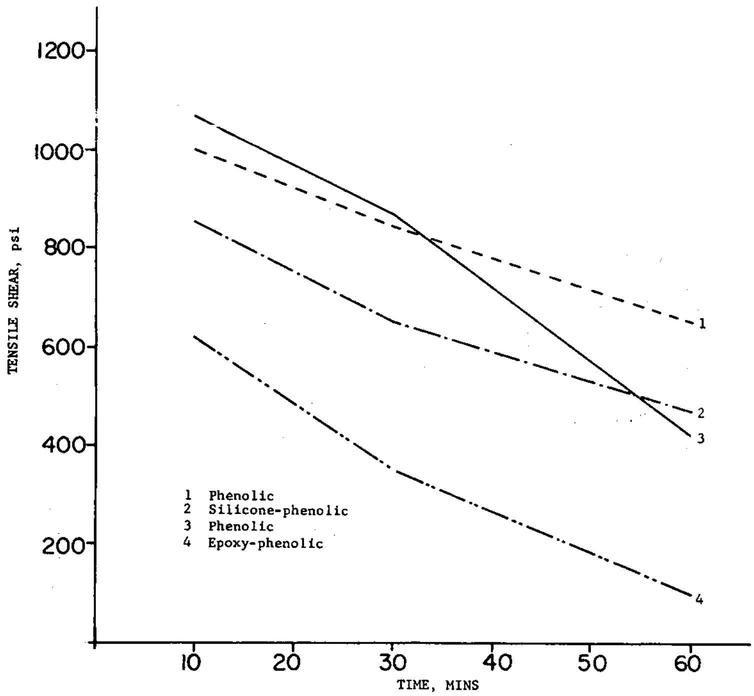

Fig. 11. Tensile shear, 1000°F. 17–7 PH stainless steel. Phosphate etch.

A newer research area has been opened as a result of this adhesive. There are many loose ends to be gathered, including mechanism studies to determine how the inorganic compounds react with the organic polymers. Such work is presently under way and if successful, should provide a more sophisticated approach to a finished product.

Short Exposures at 700–1000°F.

At the start of the first program,[3] the best commercially available adhesives were tested at 700–1000°F. for periods of 10, 30, and 60 min. in air, on 17–7 PH stainless steel. This was done to determine the present state of the art and to find systems with the best heat stability for use as a starting point for improvement. Figures 9 to 11 show these data.

These evaluation results indicated that purely organic adhesives can do surprisingly well on steel for up to an hour at 1000°F. Of the four adhesives used, the 422-type epoxy-phenolic was the poorest under all test conditions. This was consistent with other data obtained during this program,[3] which showed that epoxies and epoxy blends gave the poorest laminates, the highest oxidation rate constants, and steepest thermogravimetric analysis curves. It seemed fairly conclusive that for the test conditions used, epoxies as they are known today are incapable of satisfactory performance. At this point, epoxies were eliminated from further consideration.

The 700°F. data were interesting in another way. Tensile shear strengths after an hour were higher than after 10 min. for all but the epoxy-containing adhesive. This is thought to be due to a continuing postcure at a temperature which is not high enough for the degradation reactions to outweigh the crosslinking reactions. As the exposure temperature was increased, the hour values became lower than the 10-min. values.

This review of recent work in high-temperature adhesive research briefly described the work leading up to current developments and gave some data on the present status of this area. Generally, the picture appears hopeful but does show some areas that require increased effort in the future.

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Synopsis

(*1*) The prognosis for adhesives useful up to an hour at 1000°F., in air, is good. (*2*) Organic adhesives based on phenolic and silicone-phenolic resins are more capable than expected of usefulness at 1000°F. (*3*) Preparation of semi-inorganic adhesives by reaction of heat stable organic polymers with inorganic reagents is feasible. (*4*) The prospect appears excellent for the achievement of adhesives to be used for 1000 hr. at 500°F., in air, on steel. (*5*) Despite research on 2000°F. adhesives, effort is still urgently needed on materials for use at lower temperatures. (*6*) Perhaps the area with the most serious shortage of information and research is the development and testing of adhesives for use at 180–500°F. for periods of three to five years. Both military and civilian agencies are planning the construction of supersonic transports which need such structural adhesives.

Résumé

Les prévisions pour des adhésifs pouvant être utilisés à l'air libre pendant une heure à 1000° F. sont bonnes. Des adhésifs organiques basés sur des résines phénoliques et silicone-phénoliques sont capables plus qu'on ne pourrait s'y attendre d'être utilisées à 1000° F. Il est possible de préparer des adhésifs semi-organiques par réaction de polymères organiques. Les prévisions paraissent excellentes pour la mise au point d'adhésifs pouvant être utilisées à l'air libre sur de l'acier, pendant 1000 heures à 500° F. Malgré les recherches sur des adhésifs à 2000° F, un effort urgent s'impose en ce qui concerne les matières à utiliser à des températures plus basses. Le domaine, où le manque d'informations et de recherches est le plus sérieux, est celui du développement et d'essai d'adhésifs pour usage à 180° F–500° F pendant des périodes de trois à cinq ans. Aussi bien les entreprises militaires que civiles font des plans pour la construction de transports supersoniques qui ont besoin d'adhésifs structurels de cette espèce.

Zusammenfassung

(*1*) Die Aussichten fürKlebstoffe mit einer Brauchbarkeit bis zu einer Stunde bei 1000°F in Luft sind gut. (*2*) Organische Klebstoffe auf Phenol- und Silicon-Phenolharzbasis besitzen bei 1000°F eine bessere Brauchbarkeit als man erwarten sollte. (*3*) Eine Darstellung von semianorganischen Klebstoffen durch Reaktion hitzebeständiger organischer Polymerer mit anorganischen Reagenzien ist möglich. (*4*) Glänzende Aussichten bestehen für die Herstellung von Klebstoffen auf Stahl mit einer Brauchbarkeit durch 1000 Stunden bei 500°F an Luft. (*5*) Ungeachtet der Forschungsarbeit über Klebstoffe für 2000°F besteht immer noch ein dringender Bedarf für die Entwicklung von Materialien zum Gebrauch bei tieferen Temperaturen. (*6*) Den Bereich mit dem empfindlichsten Mangel an Information und Forschung bildet wohl die Entwicklung und Testung von Klebstoffen zur Verwendung über Perioden von drei bis fünf Jahren bei 180–500°F. Sowohl militärische als auch zivile Stellen planen den Bau von Überschall-Transportflügzeugen, welche derartige Strukturklebstoffe benötigen.