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Importance of Evaluation of Adhesives for All Environmental Conditions and Permanence Studies

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Introduction

One of the great contributions of some of the newer synthetic resins to adhesives has been the high degree of permanence of the resultant adhesive joints when properly made. New polymers can be tailored to provide a great variety of properties in adhesives, including high chemical stability and general resistance to bond deterioration under various service conditions. Such service might involve short- or long-term exposure at rather mild interior conditions or continuous exposure to outdoor weathering in some of the worst climatic conditions in the world, often with little or no protection given by finishes or other coatings. Often actual service involves repeating cycles from one condition to another, as from one season to another.

One of the major problems for both developers and prospective users of new types of adhesives, particularly for severe use conditions is to determine the probable service life of the adhesive in joints. They would like to telescope many years of exposure into a few hours or days and yet be able to assume that their test conditions accurately duplicated use conditions. The development of accelerated permanence tests that duplicate in a short time the performance to be expected for periods of months or years still remains largely a dream, although some progress is being made.

Discussion

Causes of Joint Deterioration

Adhesive joints may deteriorate because of any of several different types of changes or by combinations of them. These include the effects of water or water vapor, heat, biological influences, or any number of chemicals. Actual changes may be physical, chemical, or both. Often it has been difficult or impossible to determine whether physical or chemical changes are involved in observed deterioration of bonds. There is a need for much fundamental research on the mechanisms and kinetics of deterioration of various adhesive systems. Basic information here would be of immense value both to point the way to new, more durable adhesives, and to develop accelerated permanence tests that would really simulate actual service.

Early Experience with Permanence Tests

In the past, the number of different chemical systems used in adhesives for long-term service was fairly small. New synthetic resin adhesives were introduced slowly and rather cautiously, and there was generally time to start long-term exposures of joints to controlled laboratory conditions or to actual weathering to demonstrate relative performance for a few years before any real use of these new adhesives was begun. Indeed it was usually necessary to conduct and publicize results of such long-term tests before manufacturers would attempt to use the new adhesives and before the customer would accept such bonded products.

A good example is the plywood industry, which had beeen founded on the use of starch and protein-base adhesives. Urea-resin and phenol-resin glues had been introduced in this country in the mid 1930's. Their use, however, did not reach any substantial magnitude until World War II, and there had thus been several years during which outdoor weathering and controlled laboratory tests could be conducted and results analyzed. Results of such permanence studies are summarized in a U. S. Forest Products Laboratory Report.[1] These long-term tests are being continued and expanded as new types of wood adhesives are announced. These tests have established the overall superior durability of wood joints made with phenol-, resorcinol-, and melamine-resin glues for serviceability over periods of many years of unprotected outdoor weathering. Indeed these glues, when properly used, will produce joints that will outlast untreated wood of most domestic species, and in the case of the phenol- and resorcinol-resin glues will at least equal the performance of many species treated with typical wood preservatives.

It has been shown that these phenol-, resorcinol-, and melamine-resin glues are resistant to continued or intermittent exposure to temperatures up to 200°F. and to water and high humidity at this and lower temperatures. Other conventional wood glues, such as urea resins and casein or animal glues, lose much of their strength in a few months at such temperatures and humidities. The most widely used short-term test of wood glues to judge permanence under severe conditions is a boil-dry cycle prescribed in numerous specifications.[2,3] This procedure is often criticized as too severe on the basis that no one ever boiled an airplane or a boat. If one is to accelerate the effects of heat and humidity and condense the time scale from several years to a few hours, however, it is essential that seemingly extreme conditions be used. Currently, serious attention is being directed to boiling bonded wood specimens in water for 48 to 72 hr. or steaming them at atmospheric pressure for 4 to 8 hr. as more adequate short-term tests. How applicable or reliable such tests will be for new wood adhesives of different chemical types, such as epoxy resins, remains to be established.

One factor learned from earlier studies of permanence of wood joints is the importance of mechanical stresses superimposed on joints that are exposed to other deteriorating influences, such as heat, moisture, or microorganisms. Wood swells and shrinks with changes in moisture content, as do metals with temperature changes. Dimensional changes in wood across the grain are much greater than parallel to the grain. In plywood, where the grain of adjacent plies is at right angles, maximum dimensional changes, and hence maximum internal stresses, are exerted on glue lines while the plywood is subjected to high and low moisture conditions. This is one important reason for the cycles of boiling and drying or high and low humidity cycles often used in preference to continuous exposure. The vacuum-pressure soaking and drying procedure used to evaluate performance of glue joints in laminated wood timbers[4] is an example of this. Such internal stressing is more a measure of how well the gluing procedure was followed than of resistance to physical or chemical deterioration. In this test it is assumed that the adhesive is of a chemical type whose long-term durability has been previously established. In actual service of glued wood structures, external stresses are often superimposed on these internal stresses due to dimensional changes in the adherend, as well as the actual deteriorating influences that cause physical and chemical changes in the glue line itself. This principle of superimposed stresses is under study also in permanence evaluations of metal bonds.

Bonding Conditions and Joint Permanence

In any evaluation of joint quality, it is recognized that initial quality will depend both on the adhesive used and on the conditions under which the bonding is accomplished. There are many examples of the use of an adhesive of unquestioned permanence where joints have been of unsatisfactory quality. Often initial joint tests were adequate, but joints failed within a few months. This is typical of glued joints in wood furniture that hold together during final manufacture and during warehousing and sales and then open up during the first few months in the customer's home. The cause can often be traced to a seasonal change in moisture content of the wood, as from summer to winter.

Such changes result in differential dimensional changes and excessive internal stresses on the inadequately bonded joints without any evidence of physical or chemical deterioration in the adhesive itself. Thus, experimental studies of permanence of adhesive-bonded joints must be conducted to distinguish between actual deterioration and inadequate bonding conditions.

An adhesive-bonded joint is analogous to a chain of several links, each representing in turn the cohesive properties of one adherend, the actual adhesion between adhesive and adherend, cohesive strength of the adhesive film itself, the other adhesion interface, and the cohesion of the second adherend. Failure of any one link results in failure of the joint. Hence it is important to distinguish between the various sites of joint failure in interpreting test data for permanence studies.

Studies of Adhesive Films

One might question the desirability for studying the permanence characteristics of films of an adhesive entirely separate from adherends and joints, such as films cast on glass or on fluorinated hydrocarbon plastics. Limited work along these lines has been attempted from time to time. One main obstacle has been the unavailability of meaningful criteria to observe and characterize changes in such films during aging that can be correlated with actual changes in the joints themselves. At present, changes in actual joint quality in some sort of a mechanical test specimen are the only suitable procedures, but possible use of newer instrumental analysis on such isolated films should continue to be studied.

In such studies of isolated cast films, any possible influences of the adherends on the properties of the adhesive film are neglected. There is considerable empirical evidence to suggest that adherends may have important effects on the adhesive film through possible orientation, changes in solvent activity, catalytic chemical effects at the interface, and mere alterations of the time-temperature-pressure conditions used to convert the fluid adhesive to the cured solid state. Such influences of the adherends could be approximated by forming joints in the usual way and then dissolving or otherwise destroying the adherends without affecting the film itself. This is fairly easy to do with metals such as aluminum and very durable adhesives. The effect of such treatment on the film is still questionable, and better means of evaluating changes on the resultant film are needed.

Nondestructive Tests

Nondestructive tests on joints would be very useful for measuring changes in joints during periods of exposure to various environmental conditions. The same specimen could be tested repeatedly at intervals during exposure, thus eliminating problems that arise with statistical sampling of large numbers of specimens to be destroyed at intervals, as is presently done in permanence tests. Dietz and co-workers[13] have used an ultrasonic test procedure to study metal tensile specimens exposed to heat. There still remains the question of whether such repeated ultrasonic conditions affect the joint itself and whether such a nondestructive test can adequately disclose small changes in joint quality with different adherends and adhesive systems.

Weathering Tests of Bonded Metal Joints

Suprisingly, metal-bonding adhesives were used for several years in structural and semistructural applications in aircraft and other military uses before any extensive studies of the permanence of such joints were made. Two reasons cited for this were (*1*) that the chemical types of resins in such adhesives, such as phenol resins and synthetic rubbers, were known to be durable in nonadhesive uses; and (*2*) because the end use conditions of the plane were not severe and service life was likely to be short because of rapid obsolescence.

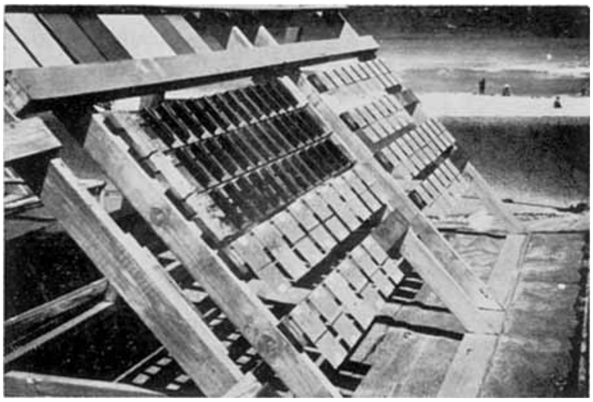

Fig. 1. Aluminum lap joint panels stressed in bending over steel bending frames

In 1953, a series of exposure studies was begun at the U. S. Forest Products Laboratory, in cooperation with the Air Force, to study the performance of a series of five commercial adhesives in aluminum lap joints when exposed to unprotected weathering at Fairbanks, Alaska; State College, New Mexico; Madison, Wisconsin; Miami, Florida; and the Panama Canal Zone. Tests included exposure to each of several controlled laboratory conditions in an attempt to get some correlation with exterior exposure that might suggest some fairly short-term laboratory tests for screening future adhesives, and inclusion in adhesive specifications. This series of studies was later expanded to include a total of 12 adhesives, with principal emphasis later restricted to the two most severe exposure sites, Miami and the Canal Zone.

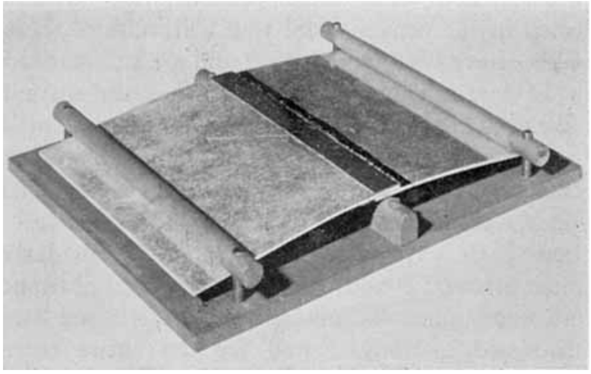

Fig. 2. Exposure installation of lap joint aluminum panels at Miami, Florida

TABLE I

Results[a] of Shear Tests[b] of Specimens from Adhesive-Bonded Lap Joint Aluminum Panels[b] after 36 Months of Exposure to Weather in Florida and the Panama Canal Zone

				Results of tests after 36 months			
				Unstressed panels		Stressed panels[c]	
Code	Type of adhesive	Control strength, psi	Exposure site	Joint strength, psi	Strength retained, %	Joint strength, psi	Strength retained, %
1	Liquid acrylic	3385	Florida	758	24	0	0
			Panama	1922	54	518	15
2	Liquid acrylic	5524	Florida	4357	79	1053	19
			Panama	5602	105	4123	72
3	Liquid vinyl-phenolic	5635	Florida	3495	62	0	0
			Panama	5405	96	4295	75
4	Liquid primer plus film, vinyl-phenolic	4410	Florida	3456	78	0	0
			Panama	4377	97	4322	95
5	Unsupported film, vinyl-phenolic	4391	Florida	4260	97	2765	60
			Panama	3523	83	3855	87
6	Liquid primer and unsupported film, acrylonitrile-phenolic	3983	Florida	2541	65	1134	28
			Panama	3507	88	2384	60
7	Unsupported film, acrylonitrile-phenolic	3713	Florida	2783	73	2122	56
			Panama	3589	98	3251	85
8	Liquid, epoxy-elastomer-phenolic	3348	Florida	2842	89	677	21
			Panama	2832	85	1858	55

[a] Each value is the average for 12 specimens (4 from each of 3 panels).

[b] Two 4 by 9 in. pieces of 0.063-in. clad 2024-T3 aluminum alloy bonded with $1/2$ in. overlap. Exposed in the form of $7\,1/2$ by $5\,9/16$ in. panels.

[c] A 0.25-in. deflection in bending at center of 6 in. span.

In this series, lap joint panels were exposed on racks at 45° from the horizontal and without any paint or mechanical protection (Fig. 1). Some of the bonded panels were unstressed, and others were under a constant stress in bending throughout the exposure (Fig. 2). Aluminum surfaces were prepared for bonding by using the standard sodium dichromate-sulfuric acid procedure, which has been shown to give best performance under salt spray conditions.[7]

After 6, 12, 24, and 36 months, panels were removed from exposure and returned to the laboratory, where shear test specimens were cut and tested in the conventional way. Results of these studies have been reported[8–11] and are summarized in Table I. These results show that the several adhesives performed somewhat differently, with the seashore exposure in Florida generally being more severe than the exposure in Panama. The epoxy-resin and acrylate-resin adhesives generally showed the greatest deterioration, particularly under stressed conditions. Certain vinyl-phenolic and epoxy-phenolic adhesives, both stressed and unstressed, performed well for the entire three years in both Florida and the Canal Zone exposures. Some of the poorer adhesive joints showed considerable evidence of metal corrosion, thus suggesting again that effects of exposure on the adherend and adhesive are interrelated.

These tests are still in progress, and a final analysis of results has not been completed.

Heat Aging of Metal Joints

In recent years much greater emphasis has been placed on the performance of adhesive-bonded joints in metals for aircraft and missiles at temperatures of 400°F. or higher for various time periods up to at least 1000 hr. This has resulted in development of entirely new organic adhesive systems. Because of the continued rise in temperature requirements, much current interest is being directed to ceramic and inorganic adhesive systems.

For performance at high temperature, two distinct problems are encountered. The adhesive may merely soften thermoplastically and lose strength without any significant chemical degradation. This is an immediate effect usually noted within a few minutes at the elevated temperature. Often the adhesive will recover much of its initial strength if cooled back to room temperature before being tested to destruction.

A more extensive problem concerns the degradation due to oxidation and related chemical changes at high temperatures. In such cases there are distinct indications that the metal adherend may have specific effects on such deterioration, effects that are characteristic of the chemical type of adhesive.[5] That is, certain adhesives, such as copolymers of butadiene and certain polyamides, perform better on corrosion-resisting steel if heat aged for 100 to 200 hr. at 500 or 550°F., whereas epoxy-phenolics are more promising on aluminum under these conditions, particularly when the adhesives are modified with certain inorganic compounds such as arsenic trioxide or manganese dioxide.

These and related findings suggest the need for considering the adhesive polymer structure and the formulation of the adhesive itself in the light of the metal adherend as a chemically active interface for performance at high temperatures, not just to assure adequate initial adhesion but to achieve good performance on heat aging.[6]

Performance of various commercial adhesives at temperatures from −100 to +800°F. has been studied[12] extensively.

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Synopsis

Although considerable research has been conducted to establish the performance of various adhesives under different conditions of service, much remains to be done. Of great importance are basic studies of the mechanisms of deterioration of adhesives in joints under known conditions so that reliable short-term performance tests may be devised to determine the expected performance of adhesives under various service conditions. Such research needs will undoubtedly be increased in importance by the continued introduction of new adhesives of different chemical types. In all probability, the nature of the adherend influences not only initial adhesion but also subsequent joint performance. Most experience reported here on permanence of joints has been gained with wood, but research on metal adhesives is also reviewed.

Résumé

Quoique de nombreuses recherches aient été effectuées pour établir la qualité d'adhésifs soumis à différentes conditions de service, il reste énormément à faire. Les études fondamentales des mécanismes de détérioration des adhésifs, sous forme de joints soumis à des conditions connues, sont d'une grande importance, de telle sorte que des tests reproductibles peuvent être mis au point pour déterminer la qualité attendue des adhésifs sous différentes conditions de service. Le caractère indispensable de telles recherches sera sans conteste accru par l'introduction continuelle de nouveaux adhésifs de types chimiques différents. En toute probabilité, la nature des adhérents influencent non seulement l'adhésion initiale mais aussi la qualité des joints ultérieurs. La plupart des expériences rapportées ici sur la durabilité des joints ont été obtenues avec du bois, mais on a également passé en revue les recherches sur les adhésifs pour métaux.

Zusammenfassung

Obwohl schon ausgedehnte Forschungsarbeiten zur Aufklärung der Verwendbarkeit verschiedener Klebestoffe unter verschiedenen Beanspruchungsbedingungen durchgeführt wurden, bleibt noch viel zu tun. Von grosser Bedeutung sind grundlegende Untersuchungen des Schädigungsmechanismus der Klebstoffe in Klebeverbindungen unter bekannten Bedingungen, die zur Aufstellung verlässlicher Kurzzeit-Beständigkeitstests zur Bestimmung der zu erwartenden Verwendbarkeit von Klebstoffen unter verscheidenen Beanspruchungsbedingungen führen. Der Bedarf an solchen Untersuchungen wird unzweifelhaft durch die fortwährende Einführung neuer Klebestoffe von verscheidenem chemischen Charakter noch an Bedeutung gewinnen. Mit grösster Wahrscheinlichkeit beeinflusst die Natur des zu verklebenden Materials nicht nur die Anfangsadhäsion sondern auch das weitere Verhalten der Verbindung. Die meisten Erfahrungen über die Beständigkeit von Verbindungen, über die hier berichtet wird, wurden an Holz gewonnen; es wird aber auch ein Überlick über Untersuchungen an Metallklebestoffen gegeben.