

Room-Temperature Curing Adhesives for Structures

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Introduction

The bonding of metals to give joints of high chemical efficiency is a difficult problem to solve for the following reasons.¹

1. Metals are nonporous and therefore any adhesives used to bond metals must not give off any volatile by-products during curing nor must they require any products from outside the joint for cure. Any material trapped in the joint during curing will be unable to escape and will cause poor joints.

2. It is very difficult to apply the adhesive to the metals in such a way that the metal is properly wetted. If no wetting of the metal surface occurs, adhesion is not obtained.

3. Adhesives for metals must have high strength both in cohesion and adhesion in order to give joints approaching the strength of the metals.

4. The adhesive must not corrode the metals.

In order for an adhesive which is cured at room temperature to meet the above requirements, it must originally be present as a liquid in either the monomeric form or as a low polymer. The process at room temperature which converts the monomer to the solid final state can be catalyzed in several ways. Among these are (a) base catalysis by moisture at the metal surface such as the alkyl cyanoacrylates² and dialkyl methylenemalonates,³ (b) incorporation of nonvolatile catalytic agents such as are employed in epoxy resins, and (c) removal of oxygen from monomeric systems stabilized by oxygen. This is the curing principle used in the MPL-monomers.^{4,5}

In this paper, the excellent adhesive performances that can be obtained on metals by judicious modifications of the physical and chemical properties of resins, curable at ambient temperatures, are presented.

Discussion

Surface-Catalyzed Adhesives

The alkyl cyanoacrylates, $\text{CH}_2=\text{C}(\text{CN})\text{COOR}'$ are prime examples of metal adhesives which poly-

merize on the surface of metals.² Whereas conventional adhesives function by the application of heat and pressure, addition of a catalyst, or evaporation of a solvent, these monomers are converted from the liquid to the solid state by polymerization when pressed into a thin film between two adherends. The process is catalyzed by weak bases such as water present on the adherend surface. Acidic substances exert an inhibitory effect on the polymerization and are used as stabilizers for the enhancement of the bulk stability of the monomers. Although quick cure, accompanied by low volume change, leads to good bond strengths, the adhesive suffers from such disadvantages as high cost, inconvenience in handling, a lack of moisture resistance, and temperature instabilities above 160°F.

Adhesives for Threaded Joints

In the field of sealants for threaded joints, polysulfide-type adhesives have found some application. Some shortcomings of these systems are short pot life, low break-out torque (BOT = 20-35 in. lb. on the basis of a 1¹/₈-in. bolt diameter), and the odor. The low BOT values with this sealant mean that fuses sealed with this have to be "staked" to insure proper alignment of the parts during storage and shipping.

The use of acrylate-type materials has been previously suggested.⁴ The treatment of a compound like MPL-monomer, normally inhibited with a small amount of hydroquinone, with a peroxide type of initiator leads to stabilization by bubbling air through the monomer. This process of "airation," evidently brings about a simultaneous activation and inhibition of the monomer such that as long as the air stream was maintained, the monomer remained fluid. In addition, metals accelerate the polymerization process. By the process of aeration an indefinitely long pot life could be expected and strong sealing action was possible with a material which could be expected to be resistant to most common solvents, acids, bases, and the action of humidity and other vapors.

Research was made into methods of either stabilizing airated MPL-monomer solutions so that no further aeration would be required or of formulating compositions that would be stable on the shelf but would polymerize in the presence of metals.⁵

After the screening of a large number of systems, control of viscosity, break-out torque, completeness of sealing within 24 hr. at 72°F. and 50% R. H., and reasonable shelf life were accomplished by investigating various compositions consisting of MPL-monomer and certain additives.

The additives chosen were substance 001 which increases the viscosity and substance 002 which hastens the rate of cure and affects the BOT values.

Subsequent work permitted the placing of 50 composition points on a BOT chart to give a more accurate picture of the relationship of BOT and composition. Figure 1 shows the areas in which the various BOT ranges may be found. A few of the contours of constant viscosity are indicated. It can be seen that, although it is not possible to prepare compositions that have all possible BOT ranges at all possible viscosities, materials can be prepared that fall within predetermined BOT limits and have a variety of viscosities.

The low viscosity preparations can be applied to the assembled threaded sections by a medicine dropper or atomizer. The high viscosity compositions can be applied by either dipping or brushing. The sealants are usable on steel, brass, copper, nickel-plated, chrome-plated, and silver-plated parts.

Room-Temperature Curing Epoxies

The principal objective of this study⁶ was to develop a low-pressure ambient temperature epoxy adhesive for field repair of metal airframes which would meet the requirements of military specifica-

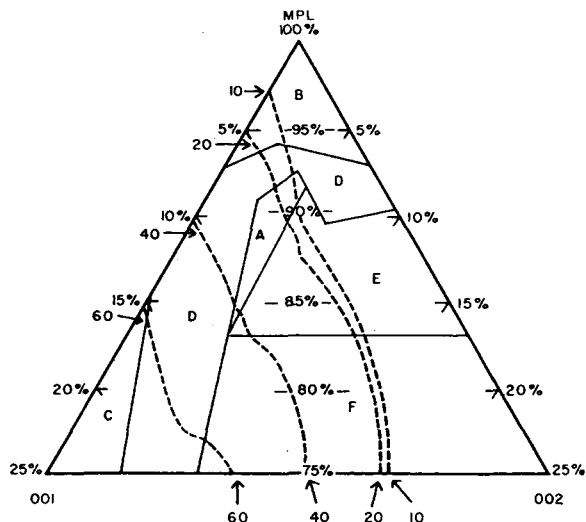


Fig. 1. Composition effect on viscosity and break-out torque. Break-out torque values (in in.-lb.): A, 33 ± 3 ; B, 31 ± 7 ; C, 25 ± 4 ; D, 19 ± 5 ; E, 8 ± 2 ; F, 5 ± 4 . (—) Break-out torque area limits. (---) Viscosity contour lines, Stokes.

tion Mil-A-5090B except for a shorter pot life of 40 min. at 80°F.

Adhesives based on epoxies are used particularly in metal and glass bonding, where advantage is taken of the ability of the epoxies to adhere well to these materials, to be cured without application of external heat, and to be alloyed with polyamides or polysulfide rubbers giving tough, impact-resistant bonds. In aircraft, epoxies have made possible metal-to-metal bonding with great savings in weight and assembly time and with improvement in the smoothness of the outside contour through the elimination of rivets.⁷

An epoxy resin is a viscous liquid or brittle solid, of no use until reacted and hardened with other materials. There are far more patents on convert-

TABLE I
Test Values on Formulation A-RT1-T(3)-M(10) Obtained at WADC on 2024-T3 Alclad Aluminum^a

Test	24 hr.	Bonds cured, ^b 120 hr.	168 hr.	Min. requirement of Mil-A-5090B
Room temp. tensile shear strength, psi	3530	3033	3374	2500
180°F. tensile shear strength, psi	1847	3477	3063	1250
-67°F. tensile shear strength, psi	487	1522	1497	2500
Room temp. bend strengths, lb.	188	132	163	150
Room temp. fatigue strength, psi	—	—	1067 (at 107 cy.)	600
Room temp. tensile shear strength after 30 days' salt spray, psi	—	—	1240	2250

^a WAC-1 cleaning method followed.

^b First 24 hr. at 73°F. under 10 psi. Rest of time at 73°F. without pressure. Pot life of adhesive was 32 min.

TABLE II
Variation in Composition of Type A-RT3 Adhesives
(Parts by weight)

Code	Thio- kol		Versamid 140	Di- ethylene- tri-amine
	LP-3	EC-3		
A-RT3-M(10)	0	3	9	0
A-RT3a-M(10)	0	3	4.5	0.5
A-RT3b-T(1)-M(10)	1	3	6	0.33
A-RT3a-T(1.5)- M(10)	1.5	3	4.5	0.5
A-RT3c-T(2)-M(10)	2	2.7	5.85	0.65
A-RT3c-T(3)-M(10)	3	2.7	5.85	0.65
A-RT3d-T(2)-M(10)	2	2.5	6.7	0.8
A-RT3d-T(3)-M(10)	3	2.5	6.7	0.8

ing the epoxide to a useful end product than on the preparation of the resin itself. The final products are thermoset; they are solids that may become soft on heating, but will never again liquefy. The greater the "density of crosslinks," the better will be the resistance to heat softening or attack by chemicals and water. In order to approach optimum salt spray resistance, an epoxide based on the novolac resins appeared to offer the best approach. These contain three or four phenolic hydroxyls per molecule and should be more resistant than the bis-phenol A type because of their higher functionality.

Previous work in this laboratory led to the formulation of an adhesive system based on an intermediate molecular weight novolac epoxy resin and having the following composition.

Component	Parts by weight
Novolac epoxy resin	20
Epon 562	5
Thiokol LP-3	3
Mineralite 4X	10
EC-3 (a tertiary amine)	3
Diethylenetriamine	1

The data obtained on this composition can be found in Table I⁸ where it can be seen that the adhesive failed to pass the -67°F . and 30-day salt spray exposure requirements of the MIL specification. Also a gel time of only 32 min. was objectionable. To improve the deficiencies of this formulation, modifications had to be made either in the components or in the cure cycle.

A new amine-terminated polyamide Versamid 140 with high heat-resistant properties was considered as a replacement for the diethylenetriamine in the above formulation. As a first step in the evaluation of this material, the amount and type of epoxy resins and filler were kept constant while variations were made in the amounts and type of amines and amount of Thiokol LP-3. The dif-

TABLE III
Effect of Substitution of Versamid 140 for Diethylenetriamine in the Converter

Formula	Run No.	Pot life, min.	Type of cure ^a	Tensile shear strengths, psi			30-day exposure to salt spray	
				73°F.	-67°F .	180°F.	Controls, psi	Av. of exposed panels, psi
				A-RT3-M(10)	135-10-1	107	A	—
			C	2210(1)	2210	—	2230, 2190	587
A-RT3a-M(10)	135-10-2	77	C	1960(1)	1200	2000(1)	2370, 2670	1017
A-RT3b-T(1)-M(10)	135-12-2	96	B	—	—	—	1930, 2310	855
			C	2230(1)	2075	—	2490, 2240	1695
A-RT3a-T(1.5)- M(10)	135-12-1	86	B	—	—	—	2150, 1880	315
			C	2470(1)	2085	—	2790, 2570	2037
A-RT3a-T(1.5)- M(10)	135-16-1	93	A	3675	1005	1690	—	—
			B	2500(1)	2085	2570	3270, 3300	2705
A-RT3c-T(2)-M(10)	135-28-1	56	E	2480(1)	2005	—	1640, 1710	1395
A-RT3c-T(3)-M(10)	135-28-2	105	E	3050(1)	2195	—	2800, 3470	1925
A-RT3d-T(2)-M(10)	135-24-1	56	A	3420	1925	1225	—	—
			B	2730(1)	2040	2220	1750, 2280	Panel fell apart in cutting.
A-RT3d-T(2)-M(10)	135-27-1	42	F	3385	3265	2110(1)	—	—
A-RT3d-T(2)-M(10)	135-41-2	50	G	3175	2140	—	—	—
			H	2610	2180	—	2950, 2580	1902
A-RT3d-T(3)-M(10)	135-43-1	50	A	—	2095	825	—	—
			B	3190(1)	1755	1735	2310, 2040	Panel fell apart in cutting.

^a Type of cure: (A) 24 hr. at 73°F . (10 psi). (B) Cure A + 120 hr. at 73°F . (no pressure). (C) Cure A + $\frac{1}{2}$ hr. at $73-160^{\circ}\text{F}$. (10 psi) + 120 hr. at 73°F . (no pressure). (E) Cure A + $\frac{1}{2}$ hr. at $73-180^{\circ}\text{F}$. (10 psi) + 120 hr. at 73°F . (no pressure). (F) 2 hr. at 212°F . (10 psi). (G) (p) 1 hr. at 212°F . (10 psi) + 16 hr. at 73°F . (10 psi). (H) (p) Cure G (p) + 120 hr. at 73°F . (no pressure).

ferent formulations that were tested are given in Table II while the results obtained can be found in Table III.

Rapid development of strength when tested at -67°F . within a 24-hr. period cure at 73°F . was a desirable feature of formulation A-RT3d-T(2)-M(10) but consistently high salt spray resistance was not obtained with any of the variations.

Complete details of all the variations made in the basic formulation cannot be described here. Some of the modifications attempted are listed below.

1. Substitution of epoxylated Thiokol LP-3 for Thiokol LP-3 gave shear strengths of 2000 psi at -67°F . after a 6-day room-temperature cure, but variable salt spray results were obtained.

was developed had the following composition:

Component	Parts by weight
Part I	
Novolac epoxy resin	20
Epon 562	5
Thiokol LP-3	3
Lead chromate	4
Mineralite 4X	6
Part II	
EC-3	3
Tetraethylene pentamine	1.3

This adhesive when cured at room temperature gave the following results on aluminum: bend strength at 73°F ., 160 lb.; shear strength after 30-day salt spray exposure, 2500 psi; shear strength

TABLE IV
The Effect of Zinc Chromate on the Physical Properties of Type A-RT3d-T(2) Adhesive

Formula	Run No.	Composition of filler	Pot life, min.	Type of cure ^a	Tensile shear strengths			Bend strengths at 73°F ., lb.	Salt spray exposure		
					73°F .	-67°F .	180°F .		Length of exposure	Controls, psi	Exposed specimens, psi
A-RT3d-T(2)-M(10)	135-24-1	10g mineralite 4X	56	A	3420	1925	1225	—	—	—	—
					2730	2040	2220	—	30 days	1750, 2280	Panel fell apart.
A-RT3d-T(2)-Z(4)-M(10)	135-100-2	10g mineralite 4X, 4g extracted zinc yellow	87	A	2955	1500	840	127, 134	—	—	—
					1905	1480	150(1)	66, 36	250 hr.	2000	Av.-1347
A-RT3d-T(2)-Z(4)-M(10)	135-101-2	4g extracted zinc yellow	105	A	2960	—	1110	136, 110, 142,	—	—	—
					1750	1090	2290	147	30 days	2000	Av.-1222 (no corr.)
A-RT3d-T(2)-Z(4)-M(10)	135-119-1	4g extracted zinc yellow	86	A	3190	—	625	160, 185, 79,	—	—	—
					—	—	—	65, 63, 58	250 hr.	1820	Av.-1232
								30 days	1820	Av.-1075 (no corr.)	

^a Type of cure: (A) 24 hr. at 73°F . (10 psi) and (B) cure A + 120 hr. at 73°F . (no pressure).

2. Inclusion of zinc and lead chromates as fillers gave lower shear strengths. However, no corrosive attack was observed during salt spray exposure (Table IV).

3. The substitution of Cardolite NC-513 for Thiokol LP-3 gave long gel times and good adhesion but lower bend strengths than with Thiokol LP-3.

4. Substitution of Alcoa 123 filler for Mineralite 4X gave lower strengths at -67°F .

At this point the inclusion of zinc or lead chromates to the basic formulation gave satisfactory salt spray resistance by ambient temperature curing. However, the strength at -67°F . was low. Heat cures of 1 to 2 hr. at 212°F . raised the shear strengths at -67°F . to 2500 psi but lowered the salt spray resistance by 50%.

In summary, the best two-part adhesive that

(73°F .), 3000 psi; shear strength (180°F .), 2200 psi; shear strength (-67°F .), 2000 psi; and pot life over 60 min.

The use of a curing agent consisting of 2.5 parts each of EC-3 and *m*-xylylenediamine gave 2800 psi at -67°F . However, strengths of only 1267 psi occurred after 30-day salt spray exposure. This drawback was readily eliminated by the use of a special hydrochloric acid-dichromate etch (Bainbridge etch).

References

- Reinhart, F. W., *Adhesion and Adhesives, Fundamentals and Practice*, Wiley, New York, 1954, p. 9.
- Coover, H. W., Jr., F. B. Joyner, N. H. Shearer, Jr., and T. H. Wicker, Jr., *Tech. Papers*, Vol. V, Fifteenth Annual Technical Conference of The Society of Plastics Engineers, 1959, p. 92.
- Halpern, B. D., J. Dickstein, R. Hoegerle, and G

Kitazawa, "A Solventless Liquid Adhesive Which Polymerizes by Catalytic Action of Surfaces to be Bonded," Borden Chemical Co., Contract No. DA-36-034-ORD-2928-RD with Picatinny Arsenal, Final Report, 1960.

4. Burnett, R. E., and B. W. Nordlander, U.S. Pat. 2,628,178 (1953).

5. Karo, W., "Investigation of Threaded Joint Sealants and Crimped Joint Sealers," Borden Chemical Co., Contract No. DAI-28-017-501-ORD with Picatinny Arsenal, Final Report, 1957.

6. Blommers, E. A., E. W. Lane, S. Loshaek, and B. D. Halpern, WADD Tech. Report 59-15, Oct. 1959.

7. Skeist, I., *Epoxy Resins*, Reinhold, New York, p. 2.

8. Discussion and tables extracted from Reference 6.

Synopsis

Methods by which synthetic adhesives can be cured at ambient temperatures are covered. The alkyl cyanoacrylates, epoxies, and MPL monomers can be cured, with little shrinkage, to obtain metal adhesive bonds which compare favorably to those obtained by high temperature modes of curing. An investigation by which novolac epoxies were rendered more flexible with accompanying increases in the temperature and salt spray resistance is described.

Résumé

On donne des méthodes par lesquelles des adhésifs synthétiques peuvent être vulcanisés à température ambiante. Les cycloacrylates d'alkyle, des époxydes et des monomères MPL peuvent être vulcanisés, avec un léger retrait pour obtenir des liens adhésifs au métal qui contrastent favorablement avec ceux obtenus par des méthodes de vulcanisation à haute température. On a décrit également une étude par laquelle des époxydes novolacs ont été rendus plus flexibles, outre une amélioration de sa résistance à la température et à un traitement par des sels.

Zusammenfassung

Verfahren zur Härtung synthetischer Klebstoffe bei Raumtemperatur werden beschrieben. Die Alkylcyanoacrylate, Epoxyde und MPL-Monomere können, bei geringer Schrumpfung, unter Bildung von Metallklebeverbindungen gehärtet werden, die den nach den Hochtemperaturhärtungsverfahren erhaltenen durchaus vergleichbar sind. Versuche zur Bildung von Epoxydnovolaken mit grösserer Biegsamkeit mit gleichzeitiger Erhöhung der Temperatur- und Salzsprühbeständigkeit werden beschrieben.