

Storage-Stable Epoxy B-Stage Resins

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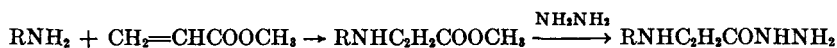
Synopsis

N-Substituted β -aminopropionhydrazides, $\text{RNHC}_2\text{H}_4\text{CONHNH}_2$, were prepared by the Michael addition of primary amines to acrylic esters. The adducts were converted to the corresponding hydrazides. The aminohydrazides react readily with terminal epoxides at moderate temperatures yielding B-stage resins of excellent storage stability. When powdered B-stage resins are sprayed on hot metal (150–230°C.), a smooth cross-linked coating is formed in less than 3 min. The coatings have unusually high elasticity, they pass the Olson button test. For best performance the amine used should have the primary amino group attached to either a primary carbon atom or directly to an aromatic nucleus. Aminohydrazides with the following R groups have been prepared: methyl, *n*-butyl, *sec*-butyl, *tert*-butyl, phenyl, cyclohexyl, benzyl, octyl, dodecyl, and octadecyl.

INTRODUCTION

Some time ago we were interested in developing storage-stable thermo-setting epoxy powders which could be applied as powders on hot metal to provide durable protective coatings. After considerable experimentation it was discovered that secondary aminohydrazides react with epoxy resins at moderate temperatures and produce B-stage resins which exhibit considerable storage stability at ambient temperatures. When these B-stage resins are powdered and sprayed on hot metal at 150–230°C, smooth, tough, elastic insoluble films are formed in less than 3 min.

A series of compounds based on the following sequence of reactions was prepared:



It was noted that for the best results the amino group of RNH_2 should be attached to a primary carbon atom or directly to an aromatic ring.

EXPERIMENTAL

All the *N*-substituted β -aminopropionhydrazides with the exception of the *N*-methyl and the *N*-phenyl compounds were prepared essentially in the same way. Aniline is a special case because it adds to acrylates only in the presence of a stronger base (triethylamine). Methyl amine has a

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TABLE I
 N-Substituted β -Aminopropionates and the Corresponding Hydrazides

| N-Substituent | Yield of ester, % | Bp, °C/ μ Hg | N, % | | Yield hydrazide, % | Mp, °C | Amine found | Number theory |
|--------------------|-------------------|------------------|-------|-------|--------------------|----------------|-------------|---------------|
| | | | Found | Calcd | | | | |
| Methyl | 45 | 30/50 | | | 97 | Liquid | 904.5 | 958.9 |
| <i>n</i> -Butyl | 70 | 80/10 | 8.37 | 8.84 | 98.3 | Near room temp | 688.8 | 705.6 |
| <i>sec</i> -Butyl | 92 | | 8.76 | 8.84 | 95.4 | " | 699.1 | 705.6 |
| <i>tert</i> -Butyl | 86.7 | 63/10 | 8.35 | 8.84 | 96.7 | " | 698 | 705.6 |
| Cyclohexyl | 91.7 | 60/60 | 7.47 | 7.57 | 100 | 82.5-83 | 605.9 | 606.5 |
| Phenyl | 87 | 93-145/ 20-50 | 7.83 | 7.82 | 95.7 | 96.5-7 | 626.6 | 626.8 |
| Benzyl | 80.1 | 92/35 | 7.16 | 7.25 | 95.7 | Liquid | 550.9 | 581 |
| Octyl | 84 | 81/25 | 6.38 | 6.51 | 96.2 | 79-81 | 509.9 | 521.8 |
| Dodecyl | — | — | — | — | 100 | 90-93.5 | 402.2 | 414 |
| Octadecyl | 101.7 | — | — | — | — | 102-102.5 | 313.2 | 316 |

TABLE II
B-Stage Resin Testing

| Reagent | Epoxy resin | | | Max temp, C° | Time of mixing, min | Remarks |
|--|-----------------|---------------------|---------|--------------|---------------------|--|
| | Amt. reagent, g | Epoxy equivalent wt | Amt, wt | | | |
| <i>N</i> -Methyl- β -amino-propionhydrazide | 15 | 525 | 185 | 130 | 2 | Powder sprayed and baked at 150°C; perfect OB in 3 min. |
| " | 8.5 | 925 | 191.5 | 140 | 2 | Powder sprayed and baked at 230°C; perfect OB in 4 min, a couple of cracks in 3 min |
| <i>N</i> -Butyl- β -amino-propionhydrazide | 22.75 | 525 | 177 | 135 | 2 1/2 | Powder sprayed and baked at 230°C; nearly perfect OB in 1 min; perfect in 2 min |
| " | 10.9 | 925 | 189.1 | 150 | 1 1/2 | Powder sprayed and baked at 150°C; nearly perfect OB in 2 hr |
| <i>N</i> -Phenyl- β -amino-propionhydrazide | 20.4 | 525 | 179.6 | 140 | 2 | Powder sprayed and baked at 230°C; perfect OB in 3 min; in 2 min 1 OB perfect, 1 passing, 1 failed |
| <i>N</i> -Benzyl- β -amino-propionhydrazide | 22.75 | 525 | 177 | 165 | 5 | Powder sprayed and baked at 230°C; perfect OB in 2 min |
| <i>N</i> -Octyl- β -amino-propionhydrazide | 25 | 525 | 175 | 130 | 4 | Powder sprayed and baked at 230°C; in 1 min some OB were perfect; in 2 min all OB were perfect |
| " | 15 | 925 | 185 | 150 | 3 | Powder sprayed and baked at 230°C; in 1 min near perfect; in 2 min perfect OB |
| <i>N</i> -Dodecyl- β -amino-propionhydrazide | 30 | 525 | 170 | 130 | 3 | Powder sprayed and baked at 230°C; in 2 min OB passed; in 3 min OB perfect |
| " | 20 | 925 | 180 | 140 | 5 | Powder sprayed and baked at 230°C; in 2 min 2 OB perfect and 1 failed; 3 min all OB perfect |
| <i>N</i> -Octadecyl- β -amino-propionhydrazide | 37.8 | 525 | 162.2 | 150 | 10 | Powder sprayed and baked at 230°C; in 1 min nearly perfect; 2 in min perfect |
| " | 24 | 925 | 176 | 150 | 5 | Powder sprayed and baked at 230°C; nearly perfect OB in 3 min |

tendency to add two molecules of acrylate and the two adducts have to be separated by fractional distillation, unless a mixture of mono- and dihydrazides is desired. The B-stage resins were prepared by mixing amino hydrazides with molten (at as low a temperature as possible) epoxy resins, mixing, cooling rapidly, pulverizing and screening through 50-mesh sieves. The epoxy resins used were the conventional bisphenol: epichlorohydrin condensation products, having epoxide equivalent weights of 500–1000.

Stability studies of the B-staged resins were made on dry powders at ambient temperatures, at 43°C and at 54°C. Stability was measured by the length generated by a 3 g resin wafer placed on a steel board inclined to a 45° angle and kept at 150°C. When the resin is crosslinked there is no further flow.

Olson button tests were conducted as follows. Cold-rolled steel panels, 3 in. × 6 in. of 14 gauge were coated to a thickness of 8–18 mils. After curing, the panel is placed in a die and given a dent 0.32 in. deep with a plunger having a loading nose of 0.50 in. radius forcing the dent from the reverse side of the panel. The film undergoes 26% extension of the surface. The perfect Olson button shows no imperfections on the surface; the passing button may have surface imperfections but no failure of the film. Failure is characterized by lack of adhesion or deep cracks extending to the metal. Three buttons are made on each panel.

Methyl *N*-Cyclohexyl-*p*-Aminopropionate and the Corresponding Hydrazide

Methyl acrylate (93 ml) was added to a rapidly stirred solution of 99 g cyclohexylamine in 100 ml methanol during 90 min at 8–15°C. The solution was allowed to stand over the weekend. The product was stripped of solvent and then fractionated *in vacuo*. The distillate came over at 60°C at 60 μ . It weighed 169.5 g, (N calcd, 7.57%; N found, 7.47%). The residue weighed 11 g, 5.7% N (calcd for diadduct 5.16% N, indicating that the residue is probably largely diadduct). The yield of the distillate was 91.6% of theory.

A 152 g portion of the distillate, 53 ml 97% hydrazine, and 50 ml of methanol were refluxed overnight at 84–85°C. The product was evaporated *in vacuo*. The residue weighed 155 g, amine number 605.4 (theory 606.5). After recrystallization from tetrahydrofuran it melted at 82.5–83°C.

Methyl *N*-Phenyl- β -Aminopropionate and the Corresponding Hydrazide

Freshly distilled aniline (93 g), 97 ml methyl acrylate, 10 ml triethylamine and 50 ml methanol were refluxed overnight. Methanol and triethylamine were evaporated. The residue distilled at 93–145°C/20–50 μ . The distillate weighed 156.5 g (87.4% theory), 7.83% N (theory for mono-adduct, 7.82% N). The residue weighed 6.5 g, 5.26% N (theory for di-adduct, 5.28%N).

To 173 g methyl *N*-phenyl- β -aminopropionate dissolved in 200 ml of methanol 50 ml 97% hydrazine was added. The reaction mixture was refluxed overnight. The product was evaporated *in vacuo*. The residue weighed 168 g (97% theory). It was recrystallized from a mixture of methanol and tetrahydrofuran; mp 96.5–97°C, amine number 626.6 (calcd 626.8).

Ethyl *N*-Methyl- β -Aminopropionate and the Corresponding Hydrazide

Methylamine (88 g, 2.84 mole) was absorbed in 1 liter of cooled tetrahydrofuran. Ethyl acrylate (216 ml, 2 mole) was slowly added with stirring during 3 hr. The temperature varied in the range 2–9°C during addition. The solution was allowed to stand overnight at ambient temperature. After stripping, the monoadduct was distilled through a 2 ft column at 30°C at 50 μ . The monoadduct weighed 115 g. The diadduct distilled at 73°C/10 μ . It weighed 120 g; the residue weighed 2 g.

Monoadduct (114 g), 25 ml methanol, and 50 ml 97% hydrazine were refluxed overnight; the product was evaporated. The residue weighed 98.5 g (theoretical 101.5 g). It was a water-white liquid, amine number 904.5 (calcd 958.9).

Table I summarizes yields, physical constants, and analytical data of the aminohydrazides.

Table II summarizes compositions, preparation, and testing of the B-stage resins. The number describing the epoxies refers to oxirane equivalents. OB refers to Olson buttons. The steel plates were preheated to the proper temperature in the oven, sprayed and put back into the oven for 1, 2, and 3 min. Maximum temperatures are the maximum temperatures reached during mixing before the melt is cooled.

Tables III and IV show storage stabilities of the B-stage resins at ambient temperature and at elevated temperatures, respectively.

TABLE III
Storage Stabilities of Epoxy-Aminohydrazide B-Stage
Resins at Ambient Temperatures^a

| Aminohydrazide | Length, in. | | | | | | |
|--|-------------|------------|-------------|-------------|-------------|-------------|-------------|
| | Initial | 1 month | 2 months | 3 months | 4 months | 6 months | 9 months |
| <i>N</i> -Butyl- β -aminopropionhydrazide | >9 | >9 | 8.375 | 5.69 | 4.44 | 1.287 | |
| <i>N</i> -Phenyl- β -aminopropionhydrazide | >9 | 8.50 | 6.625 | 6.375 | | | 6.1125 |
| <i>N</i> -Benzyl- β -aminopropionhydrazide | 8.59 | | | | | 0.81 | |

^a Epoxide equivalent weight of 525.

TABLE IV
Storage Stabilities of Epoxy-*N*-Benzyl- β -aminopropionhydrazide
B-Stage Resin at 43°C and 54°C^a

| Time, hr | Length, in. | |
|----------|-------------|------|
| | 43°C | 54°C |
| 16 | 6.34 | 2.78 |
| 24 | 6.35 | 1.81 |
| 40 | 6.31 | 0.41 |
| 72 | 4.63 | 0.11 |
| 96 | 1.41 | |
| 120 | 0.84 | |
| 148 | 0.70 | |
| 172 | 0.63 | |
| 296 | 0.4 | |

^a Epoxide equivalent weight of 525.

RESULTS AND DISCUSSION

Aminohydrazides prepared from secondary and tertiary alkyl primary amines and from cyclohexylamine gave incomplete cures in the time allotted within the temperature range used.

For all but *N*-methyl- β -aminopropionhydrazide, maximum heat distortions for the cured B-staged resins were observed when theoretical ratios of aminohydrazides to epoxy resins were used. (The *N*-methyl compound exerted a strong catalytic effect on the polymerization of epoxies and, therefore, much less than theoretical quantity was required for maximum heat distortion.)

In many cases perfect Olson buttons of maximum size were obtained, indicating that a considerable amount of fabricating can be performed on the metal after it has been coated with B-stage resin powders and cured.

Good Olson buttons were obtained from all the aminohydrazides listed in Table II.

Storage stability at ambient temperature is particularly good for B-stage resin from *N*-phenyl- β -aminopropionhydrazide. The decrease in length from 2 months' storage to 9 months' storage at ambient temperatures is virtually asymptotic.

Received July 29, 1968