Dihydrazides - The Versatile Curing Agent for Solid Dispersion Systems

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Abstract

This paper will introduce dihydrazides, a relatively obscure class of curing agents useful in virtually all thermoset resin systems. First described in 1958, by Wear, et al.[1] dihydrazides are useful curing agents for epoxy resins, chain extenders for polyurethanes, and excellent crosslinking agents for acrylics.

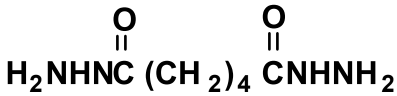
In one-part epoxy systems, depending on the backbone chain of the chosen dihydrazide, Tg's over 150°C and pot life over 6 months as cure time of less than a minute can be seen. In acrylic emulsions, dihydrazides can be dissolved into the water phase and serve as an additional crosslinker, as the emulsion coalesces and cures. As a chain extender for poylurethanes, dihydrazides can be used to increase toughness and reduce yellowing.

Introduction

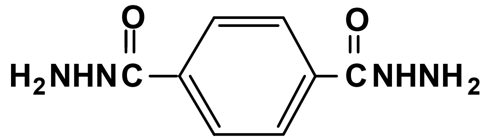
Dihydrazides are represented by the active group:

$$H_2NHN\overset{\overset{\displaystyle O}{||}}{C}(R)\,\overset{\overset{\displaystyle O}{||}}{C}NHNH_2,$$

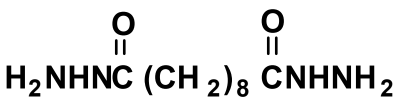
where *R* is can be any polyvalent organic radical preferably derived from a carboxylic acid. Carboxylic acid esters are reacted with hydrazine hydrate in an alcohol solution using a catalyst and a water extraction step. The most common dihydrazides include adipic acid dihydrazide (ADH), derived from adipic acid, sebacic acid dihydrazide (SDH), valine dihydrazide (VDH), derived from the amino acid valine, and isophthalic dihydrazide (IDH). The aliphatic R group can be of any length. For example, when R group is just carbon, the resulting compound is carbodihydrazide (CDH), the fastest dihydrazide. Or R as long as C-18 has been reported as in icosanedioic acid dihydrazide (LDH). Some of the more common dihydrazides are represented in Figure 1. Although hydrazine is a suspected carcinogen, the safety of ADH has been well established.[2] IDH is approved by the FDA for indirect food contact when used to cure epoxy resins under 21 CFR 175.300.



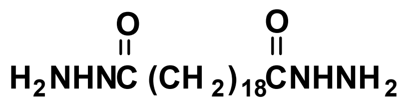
Adipic Dihydrazide (ADH)
Melting Point 180°C
Molecular Weight 175



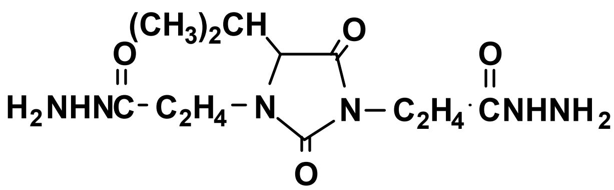
Isophthalic Dihydrazide (IDH)
Melting Point 220°C
Molecular Weight 195



Sebasic Acid Dihydrazide (SDH)
Melting Point 190°C
Molecular Weight 231



Ajicure LDH
Melting Point 175°C



Ajicure VDH
Melting Point 120°C

Figure 1. (Dihydrazide Structures and Properties)

<u>Epoxy Resins</u>

In epoxy resins, dihydrazides are typically formulated to 1/4 of dihydrazide to each epoxy equivalent. That is, all four of the primary hydrogens will react, each with one epoxy group. We have found that in our formulations, 0.7-1.2 equivalents of active hydrogen per equivalent weight of epoxide exhibit acceptable cures, with little to no reduction in properties. Cure temperature of the epoxy is related to the melt temperature of the dihydrazide. However, the dihydrazides an be accelerated with various free electron donating compounds, such as ureas, imidazoles and imidazole adducts, as well as inorganic compounds like lead octoate and stannous octoate, with some effect on pot life.

Here are some typical formulations using various dihydrazides (Table 1):

Table 1. (Epoxy Dihydrazide Formulations)

Dihydrazide exhibit a lower onset cure temperature than dicyandiamide (DICY) Dihydrazides can be accelerated in same manner as dicyandiamide. We experimented with ADH and IDH (Table 2), however the same principals hold true to all dihydrazides:

Bis-A Epoxy (EEW 190)	100	100	100	100
ADH	23		23	
IDH		26		26
Ajicure PN-23 (Imidizole - Epoxy Adduct)			3	3
Gel Time @100°C	>60	>60	14.2	23
Gel Time @120°C	>60	>60	4.7	3.8
Gel Time @150°C	10	26	2.0	1.6

Table 2. (Accelerated Epoxy Dihydrazide Formulations)

Some of the advantages of the dihydrazide epoxy combination are that they are B-stageable, allowing for use in prepregs, adhesive films, molded parts etc. Prepregs made of ADH and IDH can be B-staged at temperatures up to 165°C, and are storage stable for up to 3 months at room temperature. Cured prepregs with ADH will show a weight gain of about 2%, after 1 week in boiling water. Prepregs cured with IDH exhibit weight gains of less than 1%, under the same conditions. Lap shears at elevated temperature show little to no strength loss, and epoxies cured with dihydrazide show unparalleled toughness. Dihydrazide epoxy compounds can be formulated as flexible systems.(3)

Urethanes

Dihydrazides will cure an isocyanate through the primary amine to form the urea. This reaction is useful as chain extender and crosslinking agent for urethane coatings, adhesives and emulsions. ADH is water soluble.

We blended ADH with a mixture of an isophorone diisocyanate based urethane emulsion with a hexamethylene diisocyanate emulsion. To this blend we added 0-2% ADH, based on the total emulsion. Solvent degreased steel plates were painted with a 6-mil thick coating and dried overnight at ambient temperature and humidity. The plates were then submersed in water for 24hrs, or submitted to a Weatherometer test for 1500-hrs and 60°-gloss retention was measured. Additionally, 1/8" thick sections of the urethane film were measured for durometer hardness as well elongation. Our goals in these tests were only to show the relative performance of the ADH, not actually optimize the performance of the coating. The results of these tests can be seen in table 3.

ADH Concentration (%)	0	1.0	2.0
Water Resistance (No Change/ Swollen / Fail)	Fail (Peeled off)	No Change	No Change
Gloss Retention (%)	35	55	82
MEK Rubs	14	200	200
Shore A Hardness	35	40	50
Elongation (%)	250	150	215

Table 3. Relative Performance of ADH in Urethane Dispersion

Dabi,[4] et al. describes that dihydrazides improve the thermal oxidation color stability of polyurethanes. They made urethane emulsions of dimethyol propionic acid and hexamethylene diisocyanate, or toluene diisocyanate and chain extended these emulsions with ethylene diamine. Cast films based on these polymers yellowed at 185°C. The addition of ADH or CDH in a concentration as low as 0.25% eliminated the yellowing completely. Dabi also notes that the urethanes that are chain extended with a combination of a diamine and a dihydrazide yields superior tensile strength than either of these individual amines.

Along the same lines, Hirai,[5] et al describes the use of IDH for manufacturing leather-like coatings of solution-based polyurethanes. A combination of isophorone diamine and IDH used as a chain extender for a diphenylmethane diisocyanate (MDI) and polycaprolactone diol yields a urethane with Tg's of -40°C with excellent thermal stability as well resistance to hydrolysis and solution stability.

<u>Acrylics</u>

Dihydrazides will cure acrylics by Michael's Addition, which is a very quick reaction. Much work has been done on using water-soluble dihydrazides such as ADH and VDH. Additionally, the dihydrazides will react with the free aldehyde of the acrolein in most acrylic coating to form a pendant hydrazone. This hydrazone continues to react with other free acrolein to crosslink the acrylic polymer, as seen in figure 2.

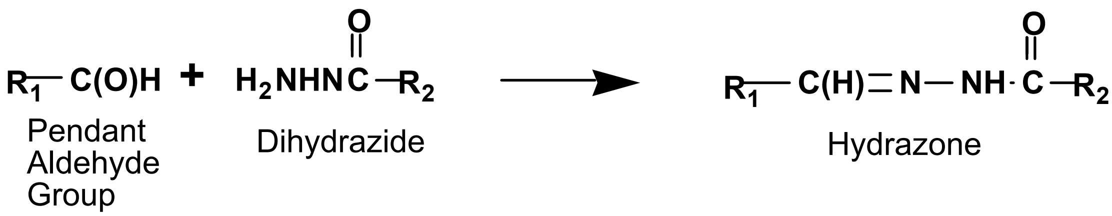


Figure 2. Half the Dihydrazide Acrylic Reaction.
R_1 is the Acrylic Backbone
R_2 is the Remainder of the Dihydrazide

Dihydrazide containing polymers show improved Wet Rub resistance and better Mandrel-bend resistance as well as improved Weatherometer Resistance.

Summary

Dihydrazides offer versatility for the formulator in preparing one-part epoxy systems. They have lower onset temperature than DICY, are fully reactive, have excellent B-stage properties, toughness and adhesion. In urethane emulsions and solution urethanes, not only do the dihydrazides offer additional crosslink density and chain extension; they reduce yellowing, which is counterintuitive to what amines normally do in urethanes. Dihydrazides offer a high measure of crosslink density for solution-based acrylic coatings.

Acknowledgements

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References

(1) US Patent #2847395. "Stable Heat-Curing Epoxy Resin Compositions." Wear.
(2) Journal of American Coll. Toxicology, "Final Report on the Safety Assessment of Adipic Acid Dihydrazide." (1994) 13(3) 154-156.
(3) US Patent #5965673. "Epoxy-Terminated Prepolymer of polyepoxide and Diamine with Curing Agent." Hermansen, et al.
(4) US Patent #4447571. "Stabilization of Polyurethanes." Dabi, et al.

(5) US Patent #4412022. "Polyurethane Compositions Prepared from a Polymeric Diol." Hirai, et al.
(6) Lee and Neville, "Handbook of Epoxy Resins." Page 10-18

About the Author

Abe Goldstein is a Director at A&C Catalysts, with responsibilities for specialty epoxy resins and epoxy curing agents. Before that, Abe was with Ajinomoto USA responsible for epoxy curing agents. Abe is a graduate of Tulane University with an undergraduate degree in Biological Chemistry and a Masters Degree in Polymer Chemistry.