

Hypro™ ATBN/Amine Compatibility Study

Introduction

Hypro ATBN reactive liquid polymers are amine terminated butadiene-acrylonitrile copolymers. An ATBN/amine compatibility study was conducted to determine the miscibility of several grades of ATBN with numerous generic amines used as curatives for epoxy resins. Therefore it supplements previous work done with Hypro 1300X16 ATBN and various epoxy curing agents of the amine variety. Those data may be found in CVC Thermoset Technologies AB-3 bulletin. 1300X21 ATBN (10% acrylonitrile), 1300X16 ATBN (17% acrylonitrile) and 1300X35 ATBN (26% acrylonitrile) were examined at rubber concentrations of 10, 20, 50 and 100 phr (parts per hundred resin) with a stoichiometric amount of amine representing a modifier/hardener package for 2-part epoxies. Viscosity and visual appearance of the ATBN/amine mixtures were used to judge the degree of compatibility of the liquid polymer with the lower molecular weight amine.

Formulating Methodology

The amines chosen for this study included 1) unmodified and modified cycloaliphatic amines, 2) polyamides and 3) aliphatic amines. In addition to the acrylonitrile differences among the various grades of ATBN, these polymers have the AEW (amine equivalent weight) ranges from 700-1100 with the following typical values for each product:

	AEW
1300X35 ATBN	700
1300X16 ATBN	900
1300X21 ATBN	1100

The amine hydrogen equivalents contributed by ATBN is not very large and particularly when it is used at a typical toughener level of 10-20 phr. Nevertheless in each recipe the amine hardener level was adjusted accordingly to account for the amine hydrogens from ATBN. As the rubber level was increased there, of course, was a greater reduction in cure agent.

ATBN was mixed with each respective amine using a standard stirring blade at room temperature and poured into glass vials. Viscosity was measured using a DV-II + programmable Brookfield viscometer, spindle number 4. One week viscosities are reported and in some cases up to eight weeks. Photographs were taken of the ATBN/amine vials placed in front of a white background with a horizontal, black line.

ATBN/Aliphatic Amines

The family of amines least compatible with all ATBN liquid polymers is aliphatic amines. Two such amines as Ancamine 1769 and Ancamine T illustrate this immiscible phenomenon quite nicely. The vials going from left to right contain Hypro 1300X21 ATBN, 1300X16 ATBN and 1300X35 ATBN also representing a progression in acrylonitrile content of 10%-26%. Ancamine 1769 is listed in Air Products' literature as an aliphatic amine adduct.

Phase separation occurred at the 10 and 20 phr rubber levels with all three grades of ATBN. Higher rubber levels of 50 and 100 phr were prepared but not shown here as an ATBN/aliphatic amine system appears to be impractical.

Hypro™ ATBN's Compatibility w/ Ancamine 1769



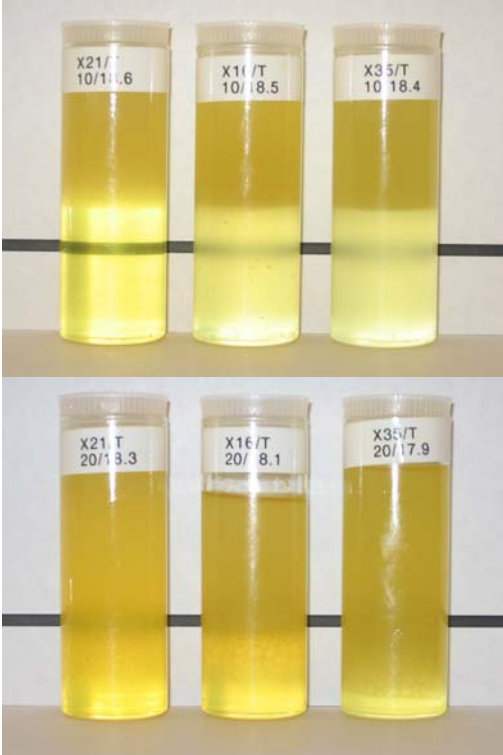
ATBN/amine	X21/1769	X16/1769	X35/1769
Ratio by weight	10/24.8	10/24.7	10/24.6
Viscosity, mPa.s at 20°C	2 phases	2 phases	2 phases

ATBN/amine	X21/1769	X16/1769	X35/1769
Ratio by weight	20/24.4	20/24.2	20/23.9
Viscosity, mPa.s at 20°C	2 phases	2 phases	2 phases

Conceivably another amine could be added to the ATBN/aliphatic amine blends to serve as a compatibilizer. However, that was beyond the scope of this study but could be considered by epoxy technologists in developing ATBN/amine modifier/curing agent systems.

Further compatibility data using Ancamine T, another aliphatic amine adduct, indicate that ATBN liquid polymers are very immiscible with it as well.

Hypro™ ATBN's Compatibility w/ Ancamine T



ATBN/amine	X21/T	X16/T	X35/T
Ratio by weight	10/18.6	10/18.5	10/18.4
Viscosity, mPa.s at 20°C	2 phases	2 phases	2 phases

ATBN/amine	X21/T	X16/T	X35/T
Ratio by weight	20/18.3	20/18.1	20/17.9
Viscosity, mPa.s at 20°C	2 phases	2 phases	2 phases

For a better appreciation of the incompatibility of ATBN with these aliphatic amines, phase separation occurred instantaneously during mixing of the polymer with the amine.

There were several degrees of immiscible rubber/amine blends observed with the extreme being distinctly separate phases of ATBN and amine. There were instances where the liquid polymer was not totally soluble in the amine with a hazy appearance scattered in the clear solution of ATBN and amine. Those less defined two-phase systems will be further reviewed in appropriate sections in this Technical Service Report.

ATBN/Cycloaliphatic Amines

ATBN liquid polymers were much more compatible with cycloaliphatic amines than with aliphatic amines. Yet certain cycloaliphatic amines were not completely miscible with ATBN so one should not state that cycloaliphatic amines are universally miscible with ATBN reactive liquid polymers. PACM is such a cycloaliphatic amine that was initially miscible with all ATBN liquid polymers but became hazy over time.

A cycloaliphatic amine very miscible with ATBN liquid polymers was Ancamine 2264. Evidenced by the stable viscosities measured up to eight weeks for the blends containing rubber levels of 10 and 20 phr these ATBN/amine blends were quite compatible.

Hypro™ ATBN's Compatibility w/Ancamine 2264



ATBN/amine Ratio by weight	X21/2264 10/27.9	X16/2264 10/27.8	X35/2264 10/27.6
Viscosity, mPa.s at 20°C, 1 WK	15,800	19,800	26,000
Viscosity, mPa.s at 20°C, 2 WK	17,800	20,200	27,400
Viscosity, mPa.s at 20°C, 8 WK	17,900	20,800	26,700



ATBN/amine Ratio by weight	X21/2264 20/27.4	X16/2264 20/27.2	X35/2264 20/26.9
Viscosity, mPa.s at 20°C, 1 WK	38,400	40,700	67,000
Viscosity, mPa.s at 20°C, 2 WK	38,700	42,100	70,500
Viscosity, mPa.s at 20°C, 8 WK	43,900	46,750	71,900



ATBN/amine Ratio by weight	X21/2264 50/26	X16/2264 50/25.4	X35/2264 50/24.6
Viscosity, mPa.s at 20°C, 1 WK	96,800	119,000	236,000
Viscosity, mPa.s at 20°C, 2 WK	105,000	117,000	245,000
Viscosity, mPa.s at 20°C, 8 WK	108,000	not measured	not measured



ATBN/amine Ratio by weight	X21/2264 100/23.5	X16/2264 100/22.4	X35/2264 100/20.7
Viscosity, mPa.s at 20°C, 1 WK	189,000	203,000	575,000
Viscosity, mPa.s at 20°C, 2 WK	193,000	201,000	not measured
Viscosity, mPa.s at 20°C, 8 WK	185,000	not measured	not measured

One of the objectives in this study was to determine the effect acrylonitrile content had on compatibility of ATBN with the amine. At the higher rubber level formulations or those at 50 and 100 phr, Hypro 1300X35 ATBN (26% acrylonitrile) provided a nice clear solution with Ancamine 2264 whereas lower acrylonitrile containing 1300X21 ATBN and 1300X16 ATBN were opaque. The viscosities of 1300X35 ATBN /Ancamine 2264 mixtures were quite high yet the increased solubility parameter of 1300X35 ATBN favored homogeneity in those compositions.

A second cycloaliphatic amine, Ancamine 2049 was quite miscible with the three grades of ATBN. Ancamine 2049 is the unmodified amine, 3,3'-dimethylmethylenedi-(cyclohexylamine).

Hypro™ ATBN's Compatibility w/Ancamine 2049



ATBN/amine Ratio by weight	X21/2049 10/31	X16/2049 10/30.9	X35/2049 10/30.7
Viscosity, mPa.s at 20°C, 1 WK	2,060	2,340	2,475
Viscosity, mPa.s at 20°C, 2 WK	2,120	2,350	2,475
Viscosity, mPa.s at 20°C, 8 WK	1,940	2 phases	2,450

ATBN/amine Ratio by weight	X21/2049 20/30.5	X16/2049 20/30.2	X35/2049 20/29.9
Viscosity, mPa.s at 20°C, 1 WK	7,150	10,200	12,400
Viscosity, mPa.s at 20°C, 2 WK	7,300	8,150	12,400
Viscosity, mPa.s at 20°C, 8 WK	6,850	2 phases	17,000

ATBN/amine Ratio by weight	X21/2049 50/28.9	X16/2049 50/28.2	X35/2049 50/27.3
Viscosity, mPa.s at 20°C, 1 WK	32,190	42,300	95,000
Viscosity, mPa.s at 20°C, 2 WK	42,000	44,000	95,000
Viscosity, mPa.s at 20°C, 8 WK	35,000	43,000	not measured



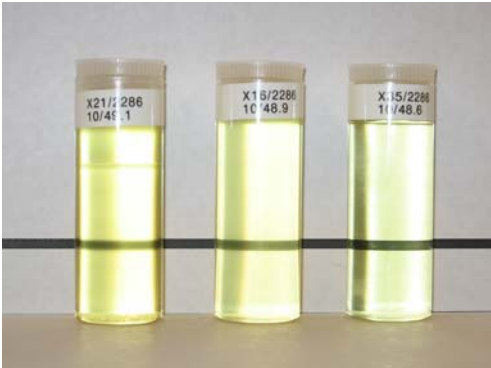
ATBN/amine Ratio by weight	X21/2049 100/23.7	X16/2049 100/21.8	X35/2049 100/23.0
Viscosity, mPa.s at 20°C, 1 WK	101,000	103,000	344,000
Viscosity, mPa.s at 20°C, 2 WK	113,000	110,000	344,000
Viscosity, mPa.s at 20°C, 8 WK	101,000	123,000	not measured

ATBN/Ancamine 2049 compositions have low mix viscosities at 10 and 20 phr rubber levels. Hypro 1300X16 ATBN (17% acrylonitrile) phase separated somewhere between two and eight weeks at room temperature. A candidate toughener/curing agent package then might be 1300X21 ATBN/Ancamine 2049 10/31 weight ratio-wise.

A third cycloaliphatic amine, Ancamine 2286 was found to be miscible with Hypro 1300X16 ATBN and 1300X35 ATBN but phase separated with 1300X21 ATBN. Low mix viscosities were achieved with the ATBN/Ancamine 2286 blends. The phase separated X21/Ancamine 2286 composition was rather unique compared to grossly incompatible ATBN/aliphatic amine systems in that there was a distinct, narrow line of demarcation between the two phases which were quite clear.

Compare, for instance X21/Ancamine 2286 to X21/Ancamine 1769 to see the significant difference in compatibility as far as phase separation is concerned noting that the former composition likely could be used with perhaps a small addition of thixotrope whereas the latter composition likely would not be useable.

Hypro™ ATBN's Compatibility w/ Ancamine 2286 (IPD/benzyl alcohol)



ATBN/amine Ratio by weight	X21/2286 10/49.1	X16/2286 10/48.9	X35/2286 10/48.6
Viscosity, mPa.s at 20°C, 1 WK	2 layers	775	825
Viscosity, mPa.s at 20°C, 8 WK	2 layers	760	820



ATBN/amine Ratio by weight	X21/2286 20/48.3	X16/2286 20/47.8	X35/2286 20/47.3
Viscosity, mPa.s at 20°C, 1 WK	2 layers	2350	2800
Viscosity, mPa.s at 20°C, 8 WK	2 layers	2320	2860

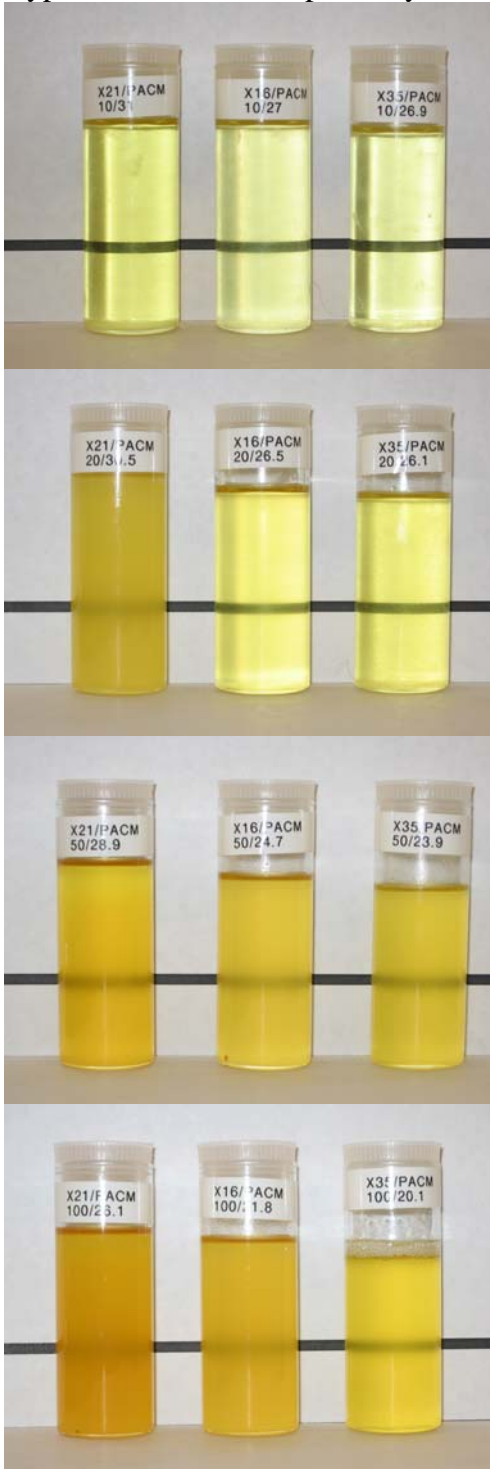
ATBN/amine Ratio by weight	X21/2286 50/45.7	X16/2286 50/44.7	X35/2286 50/43.2
Viscosity, mPa.s at 20°C, 1 WK	18,200	14,750	23,200
Viscosity, mPa.s at 20°C, 8 WK	not measured	14,700	51,100

ATBN/amine Ratio by weight	X21/2286 100/41.4	X16/2286 100/39.4	X35/2286 100/36.4
Viscosity, mPa.s at 20°C, 1 WK	61,400	54,000	114,000
Viscosity, mPa.s at 20°C, 8 WK	not measured	25,200	105,000

The final cycloaliphatic amine examined was PACM, methylene-di(cyclohexylamine). Initially it gave reasonable viscosities with all three grades of ATBN at 10 and 20 phr concentrations. However, during the aging period, there were signs of incompatibility not to the extent of an aliphatic amine/ATBN combination but noticeable nonetheless.

The ATBN/PACM systems represented a large array of miscibility relationships including clear top layer/hazy bottom layer, opaque, pockets of hazy material in a clear solution, etc. Thus the long term stability of ATBN/PACM mixtures might be a concern to someone needing a homogeneous system beyond a couple of weeks at room temperature.

Hypro™ ATBN's Compatibility w/ PACM, bis-(p-aminocyclohexyl) methane



ATBN/amine Ratio by weight	X21/PACM 10/28	X16/PACM 10/27	X35/PACM 10/26.9
Viscosity, mPa.s at 20°C, 1 WK	1,480	1,570	2,180
Viscosity, mPa.s at 20°C, 2 WK	1,550	1,650	2,100

ATBN/amine Ratio by weight	X21/PACM 20/27.5	X16/PACM 20/26.5	X35/PACM 20/26.1
Viscosity, mPa.s at 20°C, 1 WK	5,660	6,450	10,200
Viscosity, mPa.s at 20°C, 2 WK	8,100	6,400	24,000

ATBN/amine Ratio by weight	X21/PACM 50/26.2	X16/PACM 50/24.7	X35/PACM 50/23.9
Viscosity, mPa.s at 20°C, 1 WK	28,000	38,000	83,000
Viscosity, mPa.s at 20°C, 2 WK	27,000	37,500	100,000

ATBN/amine Ratio by weight	X21/PACM 100/23.7	X16/PACM 100/21.8	X35/PACM 100/20.1
Viscosity, mPa.s at 20°C, 1 WK	92,000	104,000	300,000
Viscosity, mPa.s at 20°C, 2 WK	91,400	112,000	275,000

Several polyamides were examined with the ATBN liquid polymers. Among Ancamide's 351A, 2482 and 2424 unquestionably Ancamide 2424 was most miscible with ATBN liquid

polymers. Admittedly, the viscosities were greater than those of lower viscosity amine hardeners as Ancamine 2049 yet the ATBN/Ancamide 2424 mixtures indeed appear to be solutions of butadiene-acrylonitrile liquid polymer and polyamide referring to the 10 and 20 phr rubber containing compositions.

Hypro™ ATBN's Compatibility w/Ancamine 2424



ATBN/amine Ratio by weight	X21/2424 10/58.9	X16/2424 10/58.7	X35/2424 10/58.4
Viscosity, mPa.s at 20°C, 1 WK	36,000	41,250	48,700
Viscosity, mPa.s at 20°C, 8 WK	37,000	35,500	48,900



ATBN/amine Ratio by weight	X21/2424 20/57.9	X16/2424 20/57.5	X35/2424 20/56.7
Viscosity, mPa.s at 20°C, 1 WK	55,000	56,000	91,420
Viscosity, mPa.s at 20°C, 8 WK	58,300	58,500	96,000



ATBN/amine Ratio by weight	X21/2424 50/54.8	X16/2424 50/53.7	X35/2424 50/51.8
Viscosity, mPa.s at 20°C, 1 WK	113,000	117,000	330,000
Viscosity, mPa.s at 20°C, 8 WK	not measured	not measured	not measured



ATBN/amine Ratio by weight	X21/2424 100/49.6	X16/2424 100/47.3	X35/2424 100/43.7
Viscosity, mPa.s at 20°C, 1 WK	186,000	214,000	620,000
Viscosity, mPa.s at 20°C, 8 WK	not measured	not measured	not measured

Hypro™ ATBN's Compatibility w/Ancamide 351A



ATBN/amine	X21/351A	X16/351A	X35/351A
Ratio by weight	10/51.7	10/51.5	10/51.2
Viscosity, mPa.s at 20°C, 1 WK	57,200	54,000	49,000



ATBN/amine	X21/351A	X16/351A	X35/351A
Ratio by weight	20/50.8	20/50.4	20/49.8
Viscosity, mPa.s at 20°C, 1 WK	2 layers	69,000	69,500



ATBN/amine	X21/351A	X16/351A	X35/351A
Ratio by weight	50/48.1	50/47.1	50/45.5
Viscosity, mPa.s at 20°C, 1 WK	2 layers	128,000	155,000

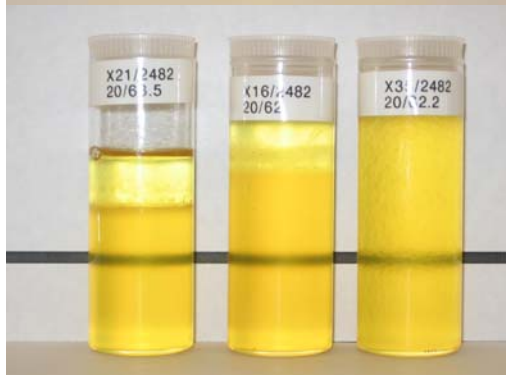


ATBN/amine	X21/351A	X16/351A	X35/351A
Ratio by weight	100/43.5	100/41.5	100/38.3
Viscosity, mPa.s at 20°C, 1 WK	225,000	244,000	580,000

Hypro™ ATBN's Compatibility w/Ancamine 2482



ATBN/amine Ratio by weight	X21/2482 10/64.6	X16/2482 10/64.4	X35/2482 10/64
Viscosity, mPa.s at 20°C, 1 WK	2 layers	24,200	22,000



ATBN/amine Ratio by weight	X21/2482 20/63.5	X16/2482 20/63	X35/2482 20/62.2
Viscosity, mPa.s at 20°C, 1 WK	2 layers	2 layers	onset of separation



ATBN/amine Ratio by weight	X21/2482 50/60	X16/2482 50/58.8	X35/2482 50/56.9
Viscosity, mPa.s at 20°C, 1 WK	2 layers	2 layers	onset of separation



ATBN/amine Ratio by weight	X21/2482 100/54.4	X16/2482 100/51.9	X35/2482 100/47.9
Viscosity, mPa.s at 20°C, 1 WK	151,000	-	390,000

Summary/Further Work:

As indicated in the introduction, this report adds to previous work associated with an 1300X16 ATBN/amine study having a similar concept. Two-part paste epoxy adhesives will be prepared from several of the ATBN/amine blends that differ in degree of compatibility to judge the importance of miscible, partially miscible and immiscible mixtures in a compounded adhesive meaning that the modifier/hardener component will be filled with a thixotrope additive and possibly a filler.

Preliminary indications are that the very incompatible ATBN/aliphatic amine blends create enormous problems when trying to mix in a thixotrope making it nearly impossible to make a paste adhesive. Even the systems that were not completely miscible gave rather low peel strength values. Therefore additional studies will be conducted using another toughening approach or CTBN (carboxyl terminated butadiene-acrylonitrile) in the form of an epoxy adduct. The inherent incompatibility of the nitrile liquid polymer with a specific amine will not be a concern as the CTBN/epoxy adduct will be added to the resin portion of a two-part epoxy. Adhesive studies will be examined in a comparative study.

Table I summarizes the compatibility results from this study. Among the three generic amines examined 1) cycloaliphatic amines are most miscible with ATBN liquid polymers and 2) aliphatic amines are least miscible with ATBN. However the compatibility issue might differ from a supplier's and formulator's perspective. In the former case long term stability of the amine hardener component may be necessary which could hinder the use of ATBN in an aliphatic amine system. In the latter case, if long term stability is not a concern then ATBN could be used effectively in aliphatic amine containing hardener compositions. That was found to be the case in some adhesives work done with an ATBN/Ancamine AD/Ancamide 350A system where high peel strength was achieved. (Note: Ancamine AD is an aliphatic amine).

Table 1. ATBN/Amine Stability at 10 and 20 phr Rubber Concentrations

		RLP					
		1300x21 10% Acrylonitrile		1300x16 17% Acrylonitrile		1300x35 26% Acrylonitrile	
		10 phr	20 phr	10 phr	20 phr	10 phr	20 phr
Aliphatic Amines	Ancamine 1769	-	-	-	-	-	-
	Ancamine T	-	-	-	-	-	-
Cycloaliphatic Amines	Ancamine 2264	++	++	++	++	++	++
	Ancamine 2049	++	++	+	+	++	++
	Ancamine 2286	-	-	++	++	++	++
	PACM	+	+	+	+	+	+
Polyamides	Ancamine 2424	++	++	++	++	++	++
	Ancamide 351A	+	-	+	+	+	+
	Ancamine 2482	-	-	+	-	+	-

Where:

- = Incompatible

+ = Compatible over short time periods (2-8 wks)

++ = Compatible over long time periods (> 8 wks)